Original Article

Novel approach of determining the best absorbent for the quantification of aqueous analyte using laser-induced breakdown spectroscopy (LIBS): Zeolite versus bentonite

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Abstract

Heavy metal pollution, particularly from sources like lead (Pb), poses significant risks to human health and the environment. Monitoring heavy metal contamination is essential, and Laser-Induced Breakdown Spectroscopy (LIBS) is a promising technique for this purpose. However, matrix effects, particularly from adsorbent materials like zeolite and bentonite, can influence the accuracy of LIBS measurements. This study aims to investigate the matrix effects of zeolite and bentonite on the measurement of Pb using LIBS. It is focusing on how the physical and chemical properties of these materials impact the detection of Pb emission lines. Zeolite and bentonite samples were prepared by grinding and sieving to obtain powders with particle sizes less than 74 µm. These powders mixed with varying weights of lead nitrate ($Pb(NO_3)_2$) and pelletized to create uniform samples. The pellets were analyzed using LIBS, employing a Q-switched Nd:YAG laser. The emitted plasma light was collected and transmitted to a spectrometer equipped with an intensified charge-coupled device (ICCD) camera. The spectral data were accumulated over 10 laser shots to ensure accuracy in detecting the elemental composition. The study found the matrix effects from bentonite and zeolite have significant influence on the intensity and clarity of Pb emission lines. Matrix effects on bentonite indicated a stronger influence on Pb detection compare to zeolite. It mainly due to the presence of Fe and Ti, which is affected the Pb I lines at 405.8 nm and 368.3 nm. In contrast, zeolite exhibited fewer interferences, but the matrix effect was still obvious. These matrix effects-derived interreferences can be associated with the physical and chemical properties of the adsorbents. Further research into different adsorbents and their matrix effects is warranted to improve the accuracy of LIBS in heavy metal analysis.

Keywords: Bentonite, laser spectroscsopy, LIBS, matrix effect, zeolite

Introduction

Heavy metal pollution, whether derived from natural sources or human activities, is a serious problem that must be addressed immediately because it has a negative impact on human's life [1,2]. To overcome the problem, it is necessary to carry out intensive monitoring of heavy metal content, especially on water where it become a medium for transporting heavy metals to various ecosystems. Laser-Induced Breakdown Spectroscopy (LIBS) is a reliable analytical technique for elemental analysis. It can be easily operated, has low maintenance costs, and can be used for

Received: September 11, 2024 - Accepted: September 21, 2024 - Published online: September 25, 2024

metal detection [3]. The technique is robust and can detect heavy metals even in trace levels [4]. However, the application of LIBS in analyzing liquid samples has several obstacles due to plasma quenching caused by the soft sample surface [5,6]. In addition, water samples can evaporate and produce sparks, thus preventing the capture of emission signals by optical fibers [7]. Therefore, additional modifications are needed during the sample preparation, for instance by converting the liquid sample into a solid form (liquid-solid conversion).

Liquid-solid conversion via adsorption can be carried out using various adsorbent materials which are divided into inorganic and organic materials [8,9]. Natural inorganic materials such as zeolite and bentonite have been widely reported to be functioning as adsorbents for hazardous contaminations [10,11]. In the case of heavy metals, zeolite and bentonite have been reported to effectively adsorb metals [12-14]. Some studies suggest that zeolite and bentonite have a strong affinity for heavy metal contaminants due to their mechanisms that rely on ion exchange [15-17]. Mineral ions contained in zeolite or bentonite can undergo exchange with contaminants that facilitate adsorption. The nature of both adsorbents is porous, so they have a large contact surface and high adsorption capacity. Several studies have modified zeolite or bentonite to increase their adsorption capacity [15,16]. These mineral rocks can be functionalized with organic functional groups so that they tend to have a negative surface charge that can attract more cationic heavy metals. For example, bentonite can be modified by including glutamate groups which are reported to be able to increase the adsorption of metals [18]. In addition, both zeolite and bentonite can be used as fillers in a polymer matrix [19,20]. In this case, the adsorbent filler will interact interfacial with the polymer matrix causing changes in properties (such as thermal, mechanical, or functional group properties) that benefit the adsorption process. Previous studies has been shown that using bentonite and zeolite as fillers can increase the adsorption of Pb (II) and Cr (VI) [20].

To select an appropriate adsorbent to be used in the LIBS technique, the matrix effect of the material also needs to be considered [21, 22]. It adds the ability on adsorbing heavy metals. The matrix effect refers as factors that cause deviations in LIBS analysis. The influence of the matrix can be caused by the physical or chemical properties of a material. The physical properties includes hardness, thermal properties, surface morphology and so on [23]. While the chemical properties can be hygroscopicity, hydrophilicity, presence of other elements or compounds, and so on [23]. In this study, we will examine the effect of the matrix on zeolite and bentonite on Pb measurements using LIBS. The heavy metal Pb was taken for this study because of its high toxicity and occurrence of pollution. Additionally, the spectral profile is easy to identify and study.

Methods

Materials and instruments

The tools used in this study include Thermal Gravimetric Analyzer Shimadzu DTG-60, Laser-Induced Breakdown Spectroscopy (LIBS) 2500–7, with atomic absorbance spectroscopy (AAS) (Shandon Southern A3400), grinder, 100 mesh sieve, petri dish, glass mold, blender stirrer, hot plate, oven, beaker, analytical balance, magnetic stirrer, and so on. While the materials include zeolite (montmorillonite) and Na-bentonite were procured from the local producer in Aceh, Indonesia.

Study design

We used true experimental design to investigate the matrix effects derived from the adsorbent materials in the Pb measurement using LIBS. The adsorbent materials selected were bentonite and zeolite. In the present study, no adsorption was carried out, but the analytes were only mixed in powder form, then homogenized and pelletized before being analyzed by LIBS. Pb emission lines will appear with different intensities which are thought to originate from the influence of the matrix.

Sample preparation

The adsorbents used in this study include bentonite, zeolite and the combination of both bentonite and zeolite. The ratios used for the bentonite: zeolite combinations were 2:3 and 3:2

(g/g). The adsorbents are made in powder form, with a size of <74 µm. If necessary, the adsorbent is the first ball milled before being sieved with a 200-mesh sieve. The analyte Pb (in the form of $Pb(NO_3)_2$) is mixed with the adsorbent powder, so that the concentration of the analyte in the adsorbent becomes 100 mg/kg. Afterward, the mixture was stirred until homogeneous and prepared as pellets. Then, the sample was shot with LIBS at a fix time delay and laser energy parameters to see the effect of matrix interference on the analyte (Pb) signals.

Laser-induced breakdown spectroscopy (LIBS)

The LIBS equipment was assembled similar to previous report [24]. The zeolite and bentonite pellets were analyzed using Laser-Induced Breakdown Spectroscopy (LIBS) by employing a Q-switched Nd: YAG laser (1064 nm) having a pulse width of 8 ns and a repetition rate of 10 Hz. The laser beam was directed onto the sample surface through a reflector and focused using a lens with a focal length of 150 mm, generating plasma upon ablation. To ensure uniform ablation, the pellets were rotated at a speed of 5 revolutions per minute during the process. The emitted light from the plasma was collected using an optical fiber positioned 6 cm from the side of the sample with a numerical aperture of 0.22. This light was then transmitted to a spectrometer equipped with an intensified charge-coupled device (ICCD) camera that captured the spectral data. Synchronization between the laser pulse and the ICCD camera was achieved using a digital delay generator, with the camera configured at a gate delay of of 2 µs and a gate width of 30 µs. The laser energy was set at 54 mJ, and the experiments were conducted in open air at atmospheric pressure (1 atm). The data accumulated over 10 laser shots.

Results

Effect of bentonite matrix

LIBS spectrum of the bentonite containing 0.5–1.5 g $Pb(NO_3)_2$ in the wavelength range of 200 to 900 nm is presented in **Figure 1**. The resulting spectral profile is flat and has no molecular bands. Several emission lines that were typical to bentonite include Si I (251.6 and 288.1 nm), Al I (396.1, 394.4, and 309.2 nm), Mg I (279.5 and 280.2 nm), Ca I (422.6 nm), Ca II (393.3 and 396.8 nm), K I (766.4 and 769.8 nm), and Na I (588.9 and 589.5 nm). The emergence of Pb I spectral lines (405.8; 368.3; and 283.3 nm) can be clearly observed (**Figure 2**). The 405.8 nm line has the highest intensity compared to the emission lines recorded at other wavelengths (368.3 and 283.3 nm). However, in this emission line (Pb I: 405.8 nm), the intensity is influenced by the Fe I line (406.4 nm). While the Pb I line (368.3 nm) which has the second highest intensity is influenced by the two spectral lines in their vicinity, namely, Ti II (368.5 nm). The Pb I line (283.3 nm) is the Pb emission line that is least influenced by the matrix composition in bentonite. The emission line intensities appear to be non-linear to the Pb concentration. For example, on the Pb I line (405.8 nm), the intensity produced by a sample with 1.0 grams of Pb is greater than that of a sample with 1.5 grams of Pb (**Figure 2**).

Effect of zeolite matrix

The complete LIBS spectrum of zeolite containing 0.5–1.5 grams of $Pb(NO_3)_2$ is presented in **Figure 3**. Easily distinguishable emission lines were observed at wavelengths of 251.6 and 288.1 nm (assigned to Si I line); 396.1, 394.4, and 309.2 nm (assigned to Al I line); 279.5 and 280.2 nm (assigned to Mg I). Moreover, the presence of Ca was observed through the emission lines of Ca I: 422.6 nm and Ca II: 393.3 and 396.8 nm. Emission lines emerged at 766.4 and 769.8 nm were assigned to K I and 588.9 and 589.5 nm were assigned to Na I. LIBS spectra focusing on Pb emission lines (405.8, 368.3, and 283.3 nm) are presented in **Figure 4**. The highest Pb I emission line was observed at wavelength 405.8 nm among other Pb I lines (368.3 and 283.3 nm). There was no clear effect of Fe on Pb I: 405.8 nm emission line, though the effect of Ti II: 368.5 nm was observed on Pb I: 368.3 nm. Pb I: 283.3 nm line was not affected by the lines of other elements. Although both are not affected by the matrix, the intensity of the Pb I: 283.3 nm spectral line was at least 6 times smaller than that of Pb I: 405.8 nm. Further, the intensity of Pb I: 405.8 nm increased from 8000 a.u. to 12000 and 14000 a.u. along with the increase of Pb contents (0.5, 1.0, and 1.5 grams, respectively). The Pb I: 368.3 nm line also experienced a similar increase in intensity of 3500, 5500, and 6000 a.u. Likewise, the intensity of Pb I: 283.3 nm increased from 1300, 1700, and 2600 a.u.

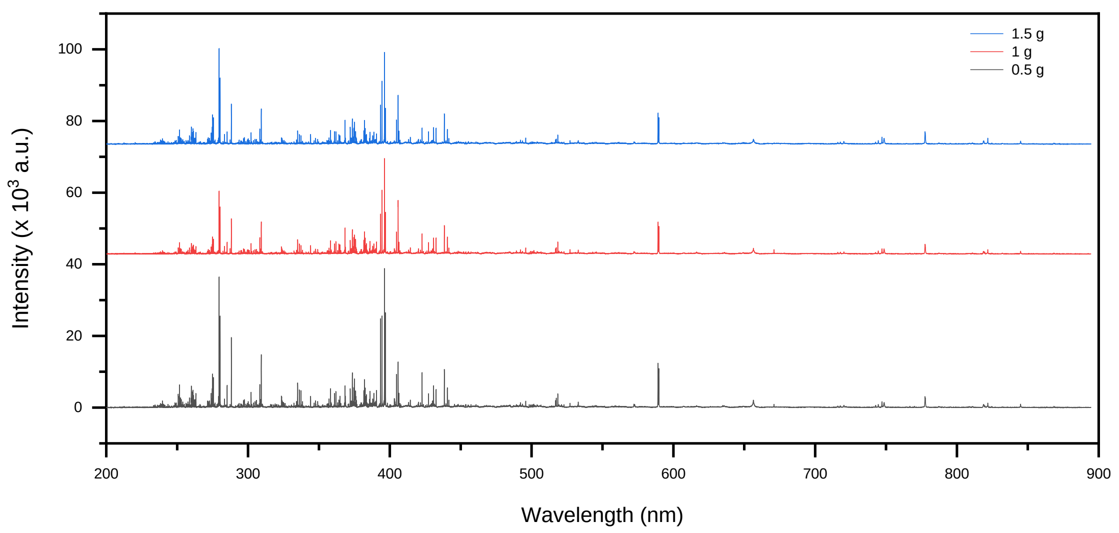

Figure 1. Complete LIBS spectra of bentonite containing Pb.

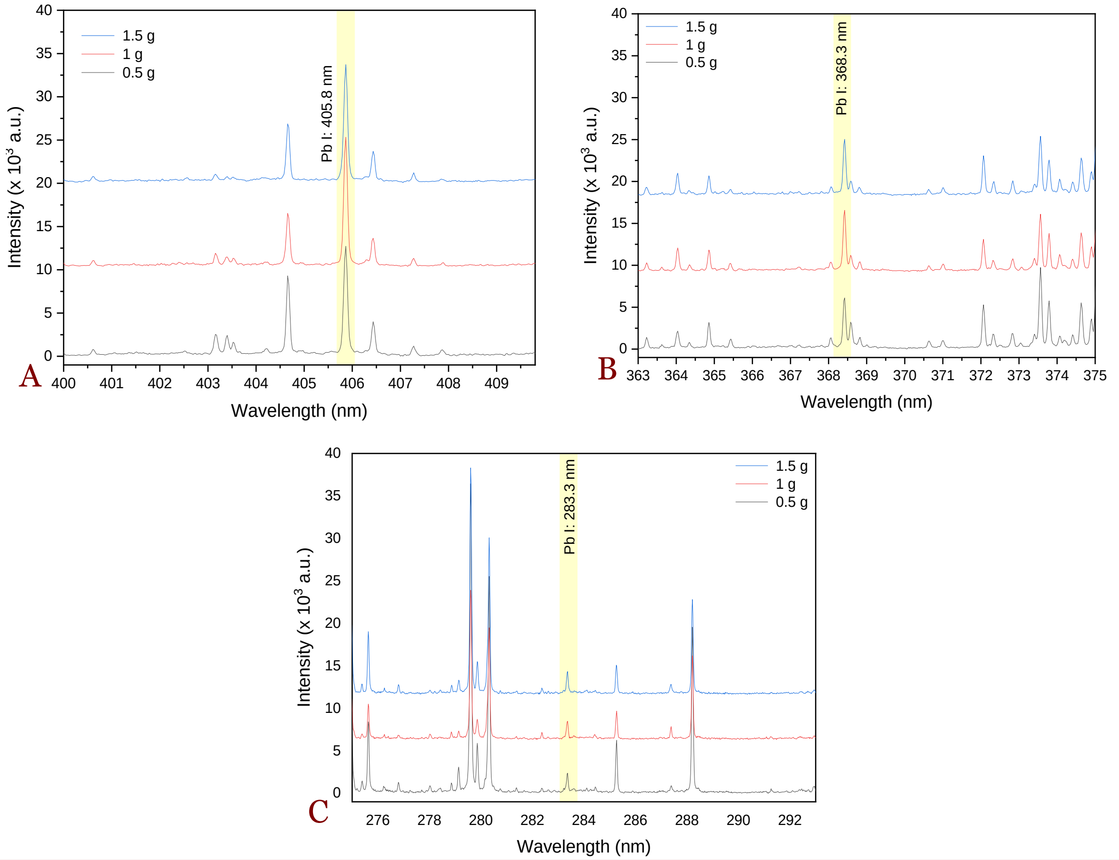

Figure 2. Pb I emission lines appear at (A) 405.8 nm, (B) 368.3 nm, and (C) 283.3 nm. Testing with bentonite samples.

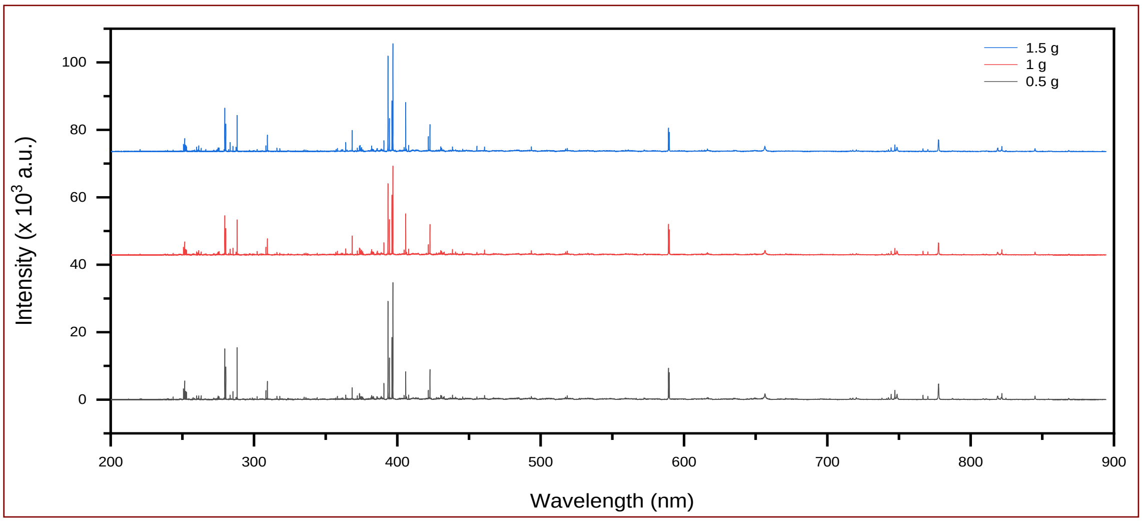

Figure 3. Complete LIBS spectra of zeolites containing Pb.

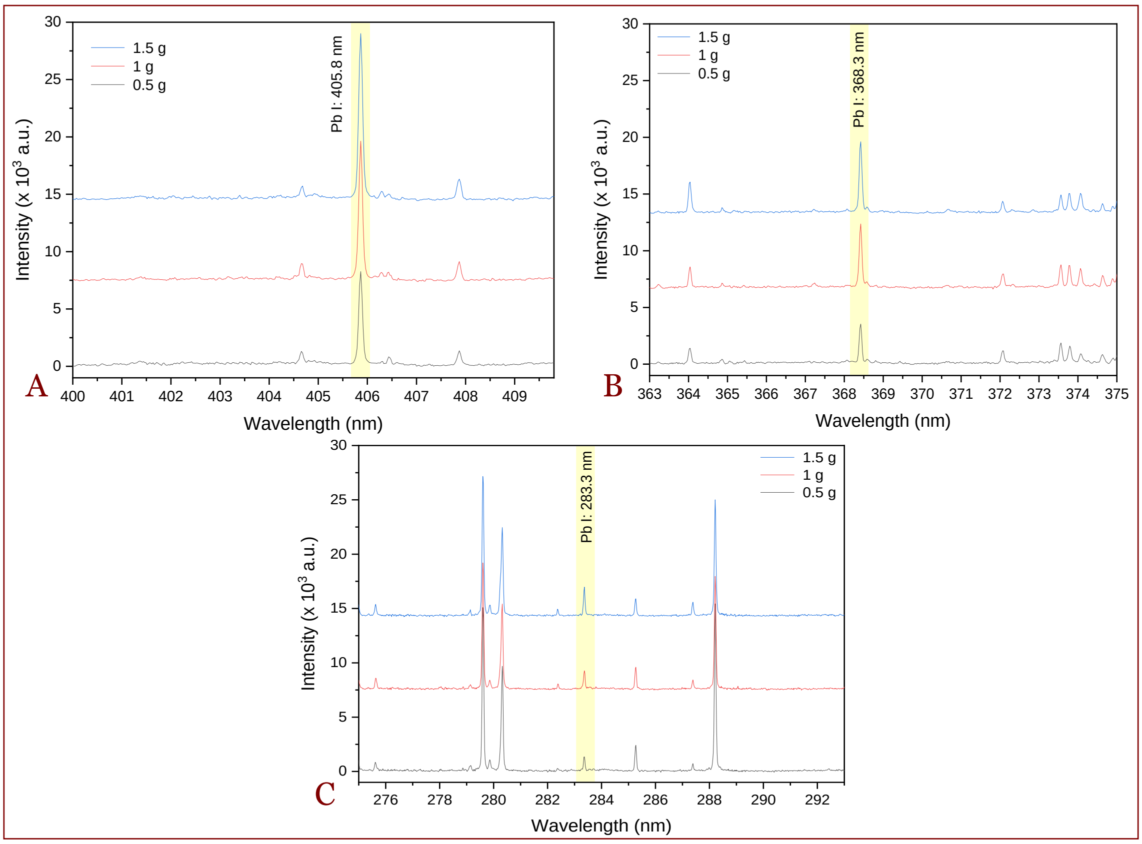

Figure 4. Pb I emission lines appear at (A) 405.8 nm, (B) 368.3 nm, and (C) 283.3 nm. Testing with zeolite samples.

Matrix effect of combined zeolite and bentonite samples

Further analysis was carried out on the combined samples of zeolite and bentonite with various ratios. LIBS spectra for bentonite and zeolite (2:3 grams) are presented in **Figure 5**. The presence of the main elements of both samples, Si, Al, Mg, Ca, K, and Na is indicated by each emission line as previously stated. Observation of the Pb emission line was then carried out at a specific wavelength range (**Figure 6**). For the Pb spectra line itself, when bentonite and zeolite were combined with a ratio of 2:3 (zeolite was made more dominant), the highest emission was shown at a wavelength of 405.8 nm, followed by 368.3 and 283.3 nm, respectively. At the lowest amount of $Pb(NO_3)_2$ (0.5 g), the intensity of the Pb I spectral lines reached 21500 a.u at a wavelength of 405.8 nm, 10500 au at 368.3 nm, and 4500 au at 283.3 nm.

Pb I: 368.3 nm line overlapped with the Ti II: 368.5 nm line (**Figure 6**). When the amount of Pb(NO_3)$_2$ was at 0.5 g, the Ti II line (368.5 nm) had an intensity that was close to Pb I (368.3 nm). Meanwhile, the emission of Pb I at 283.3 nm was not affected by other emission lines, although the baseline at Pb = 0.5 g overlapped with an unknown emission line. The emission line of Pb I: 405.8 nm increased from 7000 to 8700 and 21900 a.u. Pb I (368.3 nm) from 3200 a.u. to 3900 and 10500 a.u.; and Pb I: 283.3 nm – from 1500 a.u. to 1700 and 4700 a.u. (**Figure 6**).

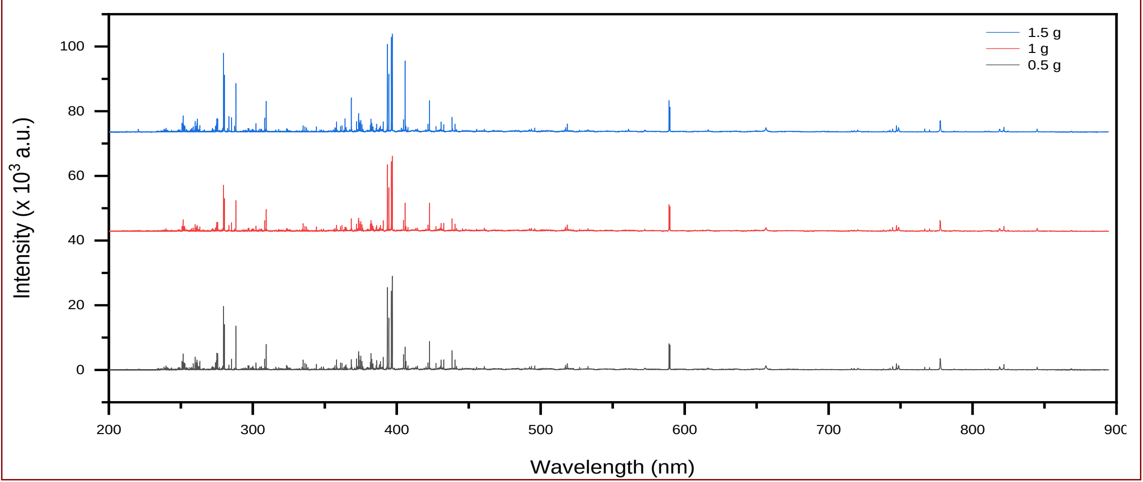

Figure 5. Complete LIBS spectra of a mixture of bentonite and zeolite (ratio 2:3) containing Pb.

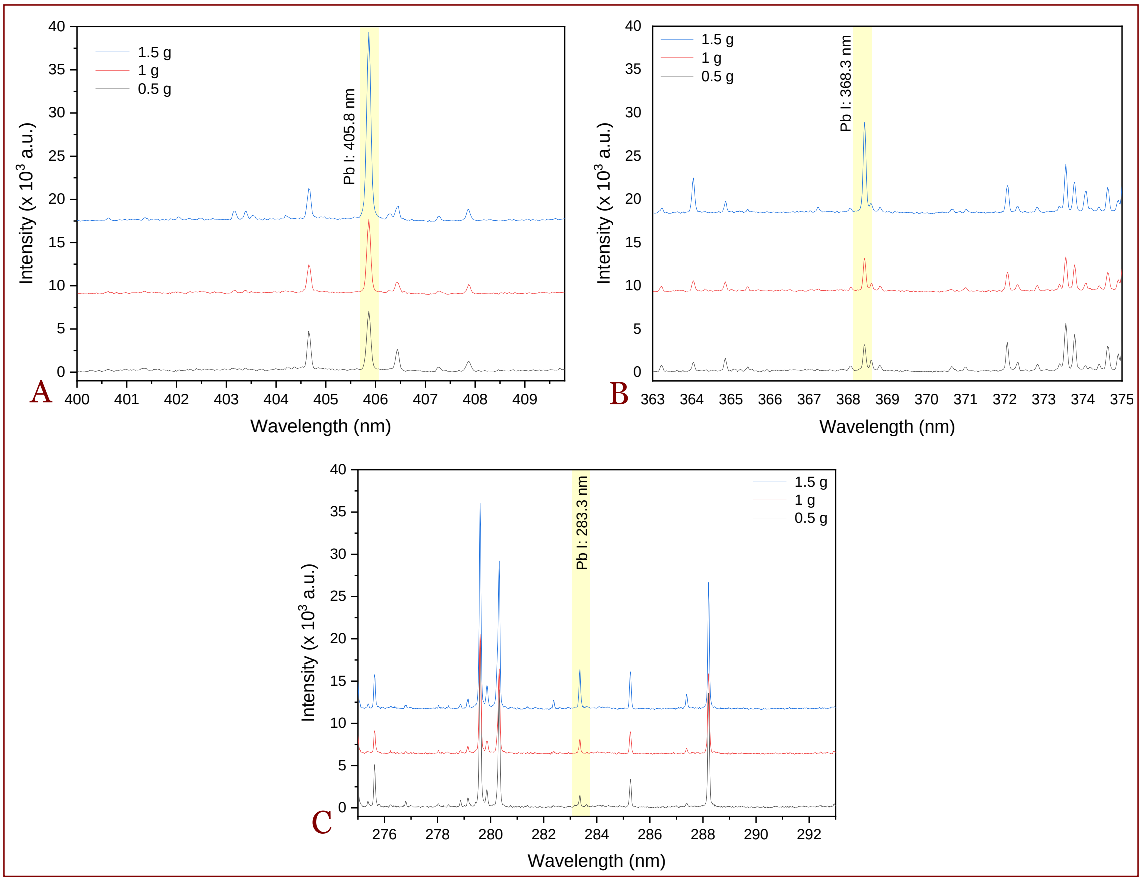

Figure 6. Pb I emission lines appear at (A) 405.8 nm, (B) 368.3 nm, and (C) 283.3 nm. Testing with a mixture of bentonite and zeolite samples (ratio 2:3).

For the case of matrix influence on the intensity of Pb emission lines from the mixture sample of bentonite and zeolite with a ratio of 3:2 (dominant bentonite), the full result of LIBS spectra is shown in **Figure 7**. The main elements contained in both types of clay can be observed in the emission lines of Si I (251.6 and 288.1 nm), Al I (396.1; 394.4; and 309.2 nm), Mg I (279.5 and 280.2 nm), Ca I (422.6 nm), Ca II (393.3 and 396.8), K I (766.4 and 769.8 nm), and Na I

(588.9 and 589.5 nm). At the highest Pb concentration (1.5 g $Pb(NO_3)_2$), Pb I (405.8 nm) reaches 14100 a.u., Pb I (368.3 nm) – 6800 a.u., and Pb I (283.3 nm) 2300 a.u. (**Figure 8**). The increase in the emission lines of Pb I from 1000, 1900, to 2300 au was observed at a wavelength of 283.3 nm; from 3200, 4700, to 6800 a.u. at 368.3 nm; and 7200, 10100, to 14100 a.u. at 405.8 nm for increasing amounts of $Pb(NO_3)_2$ of 0.5; 1.0; and 1.5 g, respectively (**Figure 8**).

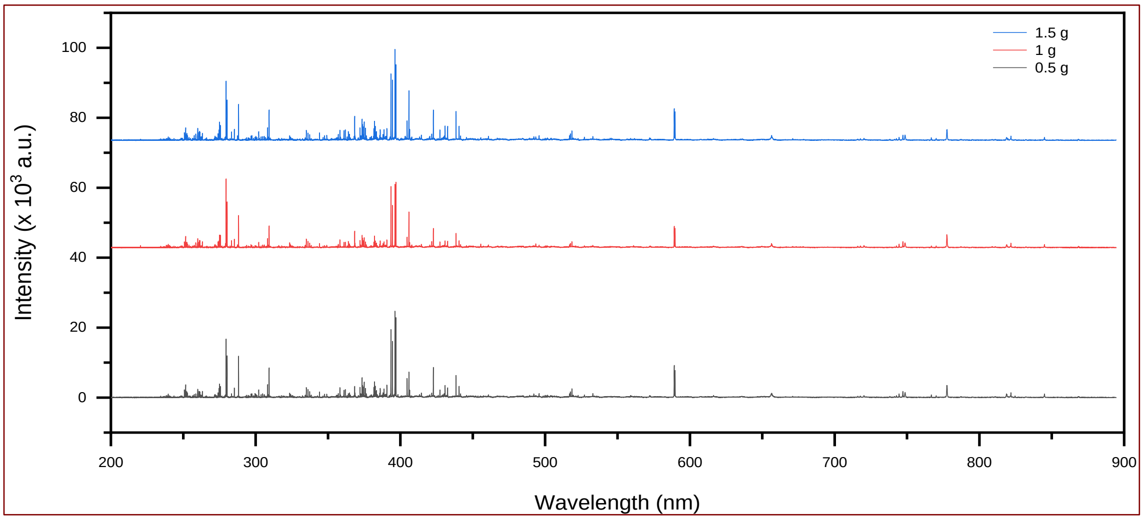

Figure 7. Complete LIBS spectra of a mixture of bentonite and zeolite (ratio 3:2) containing Pb.

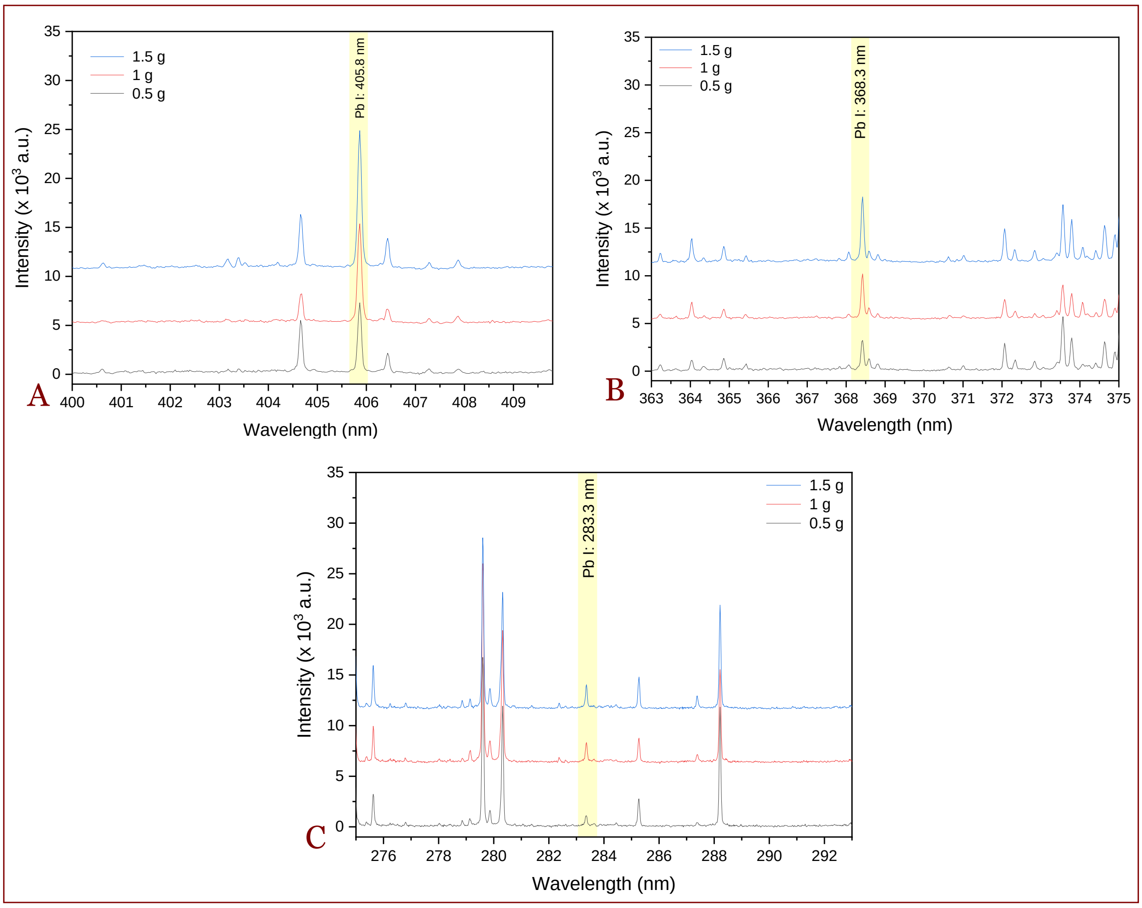

Figure 8. Pb I emission lines appear at (A) 405.8 nm, (B) 368.3 nm, and (C) 283.3 nm. Testing with a mixture of bentonite and zeolite samples (ratio 3:2).

Comparison of Pb I intensity across different samples

Comparisons of the Pb emission lines produced in each sample (zeolite, bentonite, and a mixture of bentonite/zeolite) with an amount of $Pb(NO_3)_2$ of 0.5 g are presented in **Figure 9**. In the Pb I emission line (405.8 nm), higher intensity was produced from the bentonite sample (12700 a.u.) compared to the zeolite sample (8200 a.u.), bentonite/zeolite (2:3) (7000 a.u.), and bentonite/zeolite (3:2) (7200 a.u.). For the case of Pb I (368.3 nm), the intensity sequence obtained from high to low was 6500, 3600, 3500, and 3400 a.u for bentonite, zeolite, bentonite/zeolite (2:3), and bentonite/zeolite (3:2) samples, respectively. The Pb I: 283.3 nm line has intensities (from high to low) of 2300, 1500, 1300, and 1000 a.u. for bentonite, bentonite/zeolite (2:3), zeolite, and bentonite/zeolite (3:2) samples, respectively. Thus, the highest intensity is obtained in the bentonite sample.

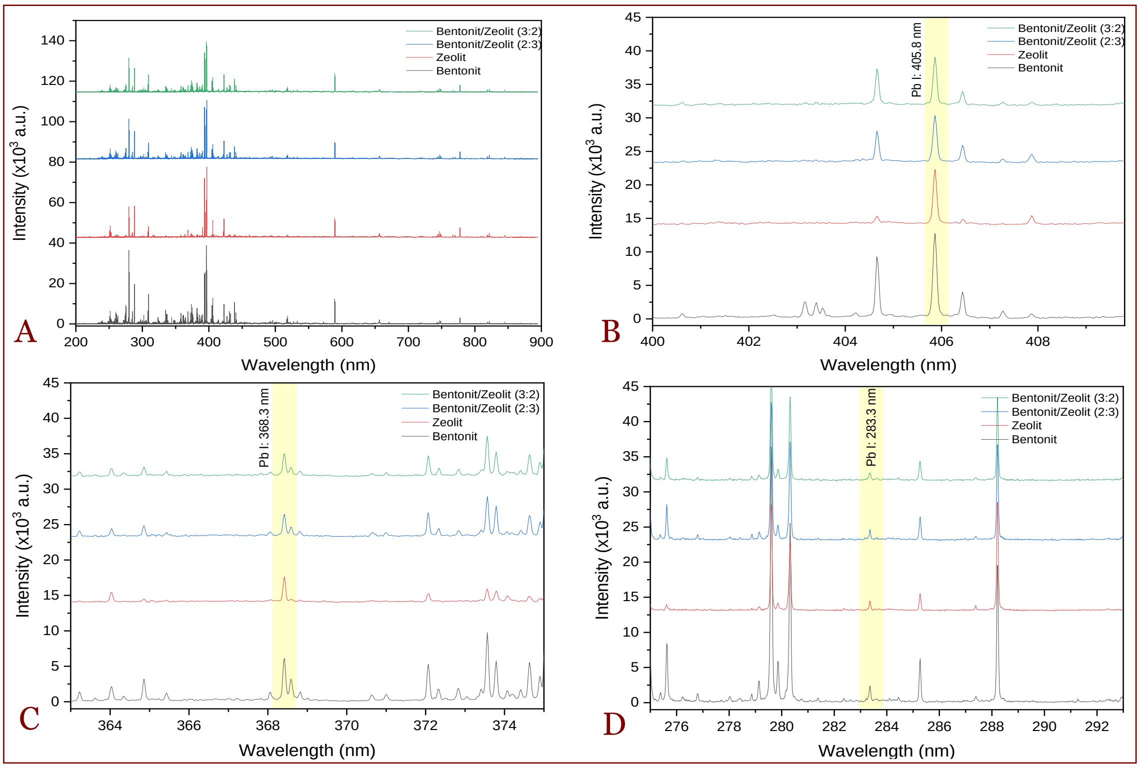

Figure 9. (A) Complete LIBS spectra of all samples containing 0.5 g of Pb. The Pb I emission lines appear at (B) 405.8 nm, (C) 368.3 nm, and (D) 283.3 nm.

The comparison of Pb emission lines in different samples was then reanalyzed for higher Pb concentrations (1.0 g Pb(NO_3)$_2$), where the spectra are presented in **Figure 10**. The intensities of the Pb I: 405.8 nm line from the highest to the lowest were 13000, 9700, 9000, and 7200 a.u. obtained from bentonite, zeolite, bentonite/zeolite (3:2), and bentonite/zeolite (2:3), respectively. While the Pb I emission line (368.3 nm), in sequence from highest to lowest, the intensity was obtained at 7200, 5600, 4700, and 3900 a.u. in bentonite, zeolite, bentonite/zeolite (3:2), and bentonite/zeolite (2:3) samples, respectively. For the Pb I: 283.3 nm line, the change in intensity was not apparent (2120, 1980, 1789, and 1734 a.u.).

At 1.5 g Pb(NO_3)$_2$, the emission line of Pb I (405.8 nm) had the intensities of 21900, 14500, 14100, 13600 a.u. for bentonite/zeolite (2:3), zeolite, bentonite/zeolite (3:2), and bentonite samples, respectively (**Figure 11**). From the highest to the lowest, the intensities of Pb I: 368.3 nm were 10500, 6800, 6600, and 6200 a.u. for bentonite/zeolite (2:3), bentonite/zeolite (3:2), bentonite, zeolite, and bentonite, respectively. The Pb I: 283.3 nm line had intensities of 4700 and 2300 a.u. for bentonite/zeolite (2:3) and bentonite/zeolite (3:2) samples, respectively. Meanwhile, for zeolite and bentonite samples, the intensities of Pb I: 283.3 nm were similar (2600 a.u.).

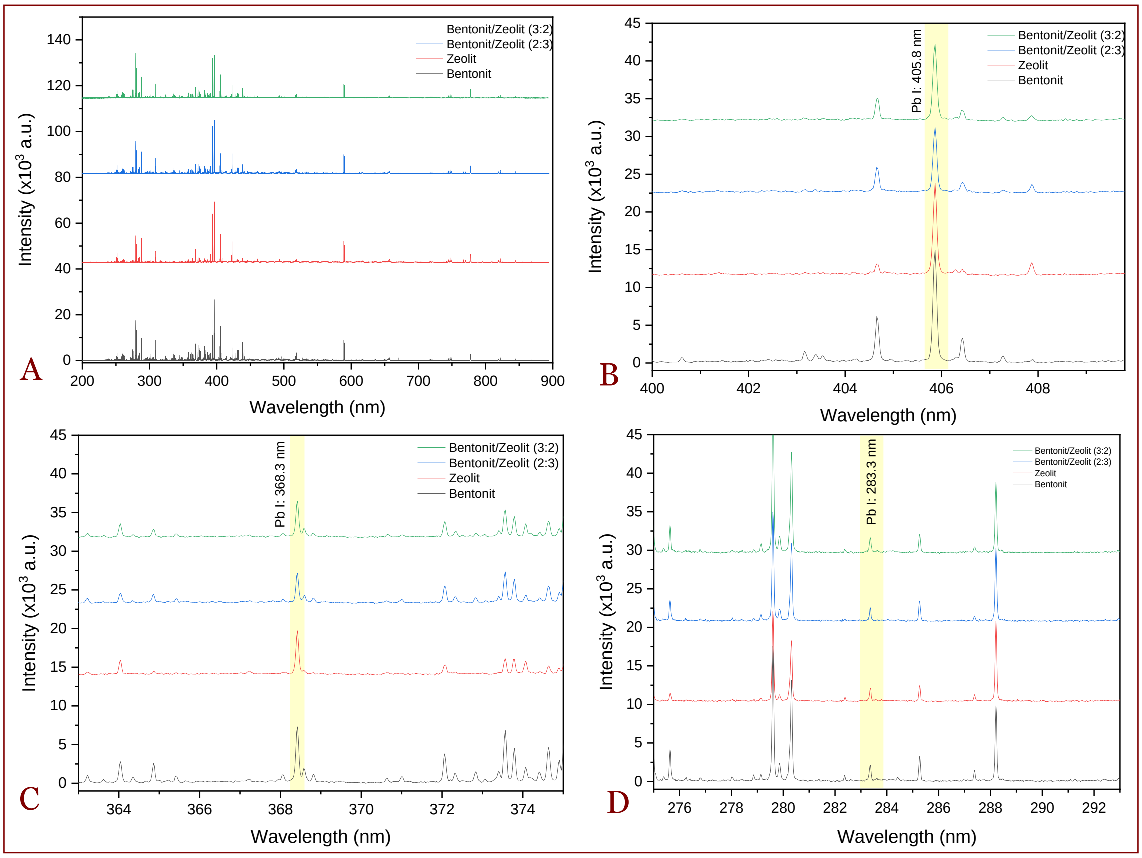

Figure 10. (A) Complete LIBS spectra of all samples containing 1 g of Pb. Pb I emission lines appear at (B) 405.8 nm, (C) 368.3 nm, and (D) 283.3 nm.

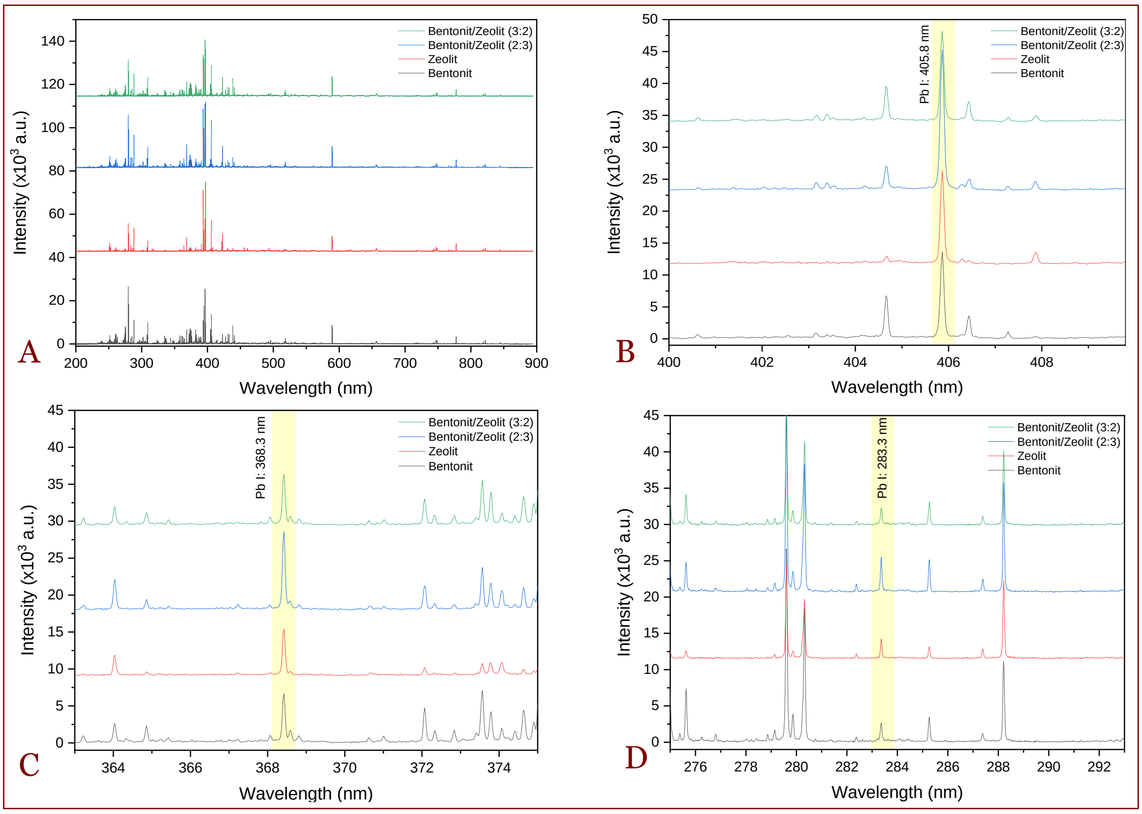

Figure 11. (A) Complete LIBS spectra of all samples containing 1.5 g of Pb. Pb I emission lines appear at (B) 405.8 nm, (C) 368.3 nm, and (D) 283.3 nm

Discussion

The resulting spectral profile of bentonite is flat and has no molecular bands, indicating that the tested sample is inorganic. Bentonite is rich in silica (Si), aluminum (Al), magnesium (Mg), calcium (Ca), potassium (K), and sodium (Na). The mineral contents in the bentonite has been confirmed in a previous study [25]. Herein, following the addition of Pb to the matrix, its presence was observed through the emergence of Pb I spectral lines at 405.8, 368.3, and 283.3 nm. Our findings also suggested that the presence of Fe and Ti in bentonite can affect quantitative analysis for Pb elements, particularly, if the emission lines Pb I: 405.8 nm and 368.3 nm were used. The influence of the spectral lines of these elements makes the Pb line unusable to determine the amount of Pb quantitatively. These elements can be referred to as a matrix that can increase or decrease the intensity of the analyte (in this case, Pb). Basically, the intensity of an element in the LIBS spectrum is determined by the amount contained in the sample. Intensity has a linear relationship to Pb concentration, which was used to construct a calibration curve [26]. However, the intensity obtained in the present study shows poor linearity because the intensity does not follow the concentration of Pb added.

The LIBS spectral profile of zeolite obtained in the present study suggest the presence of Si, Al, Mg, Ca, K, and Na, which are similar to that in bentonite. The presence of this mineral is in accordance to the previous reports [27,28]. Despite this similarity, the amount of each element is different between bentonite and zeolite [29-31]. For example, Si and Al are found more in bentonite than in zeolite, while Mg is found more in zeolite [32]. In the zeolite spectral profile herein, the Fe emission lines were not detected which is suggesting its absence or its concentration below the trace level. Other than its composition, zeolite can be distinguished from bentonite based on their structures. Zeolite has a tetrahedral TO_4 structure, while bentonite has a layered structure [33, 34]. In the present study, unlike the spectrum produced by bentonite, the Pb I line (405.8 nm) in the zeolite sample was not affected by the Fe matrix (or Fe I emission line: 406.4 nm). However, the Pb I line (368.3 nm), although smaller, was still observed to overlap with the Ti II ion emission line (368.5 nm). This indicates that the Fe and Ti contents in zeolite are significantly less than in bentonite. Thus, the presence of Ti in bentonite can affect the quantitative analysis of Pb elements.

When the matrix was prepared by combining bentonite and zeolite at ratio of 2:3 grams, the Pb I: 368.3 nm line was affected by the Ti content in the sample. Other Pb I emission lines (283.3 and 405.8 nm) were not affected. The three Pb I emission lines increased accordingly with the Pb concentration. At low Pb concentrations, Pb I emission lines had the highest intensity in the bentonite. However, the intensity was found to be the lowest in bentonite when the $(PbNO_3)_2$ content was increased from 0.5 to 1.5 g. These changes in the spectral intensities suggest the significance influence associated with the characteristics of the bentonite. The findings also suggest that the matrix effect is not always derived from the compositions of bentonite or zeolite. As previously stated, differences in structure can also act as a matrix influence.

The present study offered a novel method to select adsorbents for LIBS quantitative analysis for aqueous analytes, particularly for heavy metals. By eliminating the matrix effect, the quantification can be more accurate. However, the present study only used two adsorbents, and both adsorbents are inorganic type. Further, the analyte studied herein was only Pb. The use of this method to other analytes having different or even more complex spectral lines and characteristics is limited. Moreover, we did not employ mathematical or statistical parameters to determine the quality of the analysis. Confirmation for this method using different adsorbents and analytes, along with a more robust statistical approach, is required.

Conclusion

We observed that the matrix effects of zeolite and bentonite affecting the Pb measurement are possibly derived from the physical and chemical properties of the respective materials. The influence of the matrix effect was less in zeolite as compared to bentonite. Therefore, zeolite has a higher probability to yield accurate quantification of aqueous Pb when used to assist the LIBS analysis. Further investigation on different types of adsorbents is warranted to establish the potential of this adsorbent selection method.

Ethics approval

Not required.

Acknowledgments

None to declare.

Competing interests

Authors have no conflict of interest.

Funding

This study received no external funding.

Underlying data

All data have been presented in this article.

How to cite

Ahmad K, Prasetyo S, Zaitun Z, Hajashafira C. Novel approach of determining the best absorbent for the quantification of aqueous analyte using laser-induced breakdown spectroscopy (LIBS): Zeolite versus bentonite. Narra X 2024; 2 (2): e159 - https://doi.org/10.52225/narrax.v2i2.159.

References

1. Pratama Y, Kadir M, Rivaldi A, *et al*. Bibliometric analysis of the impact of environmental degradation on women and the importance of women's representation. Glob J Environ Sci Manag 2024;10(3):939-954.
2. Iqhrammullah M, Refin RY, Rasmi RI, *et al*. Cancer in Indonesia: A bibliometric surveillance. Narra X 2023;1(2):e86.
3. Goncharova I, Guichaoua D, Taboukhat S, *et al*. Laser-induced breakdown spectroscopy application for heavy metals detection in water: A review. Spectrochimica Acta Part B: At Spectrosc 2024:106943.
4. Parmar D, Srivastava R, Baruah PK. Laser induced breakdown spectroscopy: A robust technique for the detection of trace metals in water. Mater Today: Proceedings 2023;77:234-239.
5. Tian Y, Li Y, Wang L, *et al*. Laser-induced plasma in water at high pressures up to 40 MPa: A time-resolved study. Opt Express 2020;28(12):18122-18130.
6. Li N, Tanabe K, Nishi N, *et al*. Simultaneous detection of a submerged Cu target and bulk water by long-pulse laser-induced breakdown spectroscopy. J Anal At Spectrom 2021;36(9):1960-1968.
7. Li Z, Zhu D, Cao Y, *et al*. Rapid and ultra-sensitive trace metals detection of water by partial Leidenfrost superhydrophobic array surface enhanced laser-induced breakdown spectroscopy. Talanta 2024;273:125832.
8. Tian H, Li C, Jiao L, *et al*. Study on rapid detection method of water heavy metals by laser-induced breakdown spectroscopy coupled with liquid-solid conversion and morphological constraints. In: International Conference on Optoelectronic Materials and Devices (ICOMD 2021): 2022.
9. You Z, Li X, Huang J, *et al*. Agarose film-based liquid–solid conversion for heavy metal detection of water samples by laser-induced breakdown spectroscopy. Molecules 2023;28(6):2777.
10. Yang D, Cheng F, Chang L, Wu D. Sodium modification of low quality natural bentonite as enhanced lead ion adsorbent. Colloids Surf A: Physicochem Eng Asp 2022;651:129753.
11. Han B, Butterly C, Zhang W, *et al*. Adsorbent materials for ammonium and ammonia removal: A review. J Clean Prod 2021;283:124611.
12. Dhar AK, Himu HA, Bhattacharjee M, *et al*. Insights on applications of bentonite clays for the removal of dyes and heavy metals from wastewater: A review. Environ Sci Pollut Res 2023;30(3):5440-5474.
13. Irannajad M, Kamran Haghighi H. Removal of heavy metals from polluted solutions by zeolitic adsorbents: A review. Environ Process 2021;8:7-35.
14. Elboughdiri N. The use of natural zeolite to remove heavy metals Cu (II), Pb (II) and Cd (II), from industrial wastewater. Cogent Eng 2020;7(1):1782623.
15. Huang X, Lang L, Li J-s, Poon CS. Synthesis of Na-A zeolite loaded bentonite and its application for removal of Cu (II) from aqueous solutions. J Water Proc Engineering 2023;56:104359.

16. Pfeifer A, Škerget M, Čolnik M. Removal of iron, copper, and lead from aqueous solutions with zeolite, bentonite, and steel slag. Sep Sci Technol 2021;56(17):2989-3000.
17. Karimdad E, Bashirgonbadi M, Rahimi E. A chemo-geotechnical approach to obtain optimal mixtures of zeolite-bentonite as heavy metal adsorbents. Bull Eng Geol Environ 2021;80:1193-1203.
18. Julinawati J, Febriani F, Mustafa I, *et al*. Tryptophan-based organoclay for aqueous naphthol blue black removal–preparation, characterization, and batch adsorption studies. J Ecol Eng 2023;24(7).
19. Ahmad K, Chiari W. Metal oxide/chitosan composite for organic pollutants removal: A comprehensive review with bibliometric analysis. Narra X 2023;1(2):e91.
20. Iqhrammullah M, Marlina, Hedwig R, *et al*. Filler-Modified Castor oil-based polyurethane foam for the removal of aqueous heavy metals detected using laser-induced breakdown spectroscopy (LIBS) technique. Polymers 2020;12(4):903.
21. Wei Z, Ye W, Zhai C, *et al*. Enhancement of LIBS signal in lithium solution at the interface between liquid and an aluminum substrate. Spectrochim Acta B: At Spectrosc 2023;208:106780.
22. Iqhrammullah M, Abdulmadjid S, Suyanto H, Kemala P. A review of membrane-facilitated liquid-solid conversion: Adding laser-induced breakdown spectroscopy (LIBS) multi-applicability for metal analysis. In: Journal of Physics: Conference Series: 2021.
23. Senila M, Cadar O, Miu I. Development and validation of a spectrometric method for Cd and Pb determination in zeolites and safety evaluation. Molecules 2020;25(11):2591.
24. Iqhrammullah M, Suyanto H, Pardede M, *et al*. Cellulose acetate-polyurethane film adsorbent with analyte enrichment for in-situ detection and analysis of aqueous Pb using Laser-Induced Breakdown Spectroscopy (LIBS). Environ Nanotechnol Monit Manag 2021;16:100516.
25. Angkawijaya AE, Santoso SP, Bundjaja V, *et al*. Studies on the performance of bentonite and its composite as phosphate adsorbent and phosphate supplementation for plant. J Hazard Mater 2020;399:123130.
26. Nisah K, Ramli M, Iqhrammullah M, *et al*. Controlling the diffusion of micro-volume Pb solution on hydrophobic polyurethane membrane for quantitative analysis using laser-induced breakdown spectroscopy (LIBS). Arab J Chem 2022;15(6):103812.
27. Aulia S, Simanjuntak W, Pandiangan KD, Rilyanti M. Transformation of Lampung Natural Zeolite into Zeolite-A by Aluminium Addition and Application as Catalyst for Biomass Pyrolysis. Indones J Energy 2024;7(2):124–140-124–140.
28. Budianta W. The use of natural zeolites from Gunungkidul, Indonesia for preventing arsenic pollution of soils and plants. In: IOP Conference Series: Earth and Environmental Science: 2021.
29. Shekarchi M, Ahmadi B, Azarhomayun F, *et al*. Natural zeolite as a supplementary cementitious material–A holistic review of main properties and applications. Constr Build Mater 2023;409:133766.
30. Feng M, Kou Z, Tang C, *et al*. Recent progress in synthesis of zeolite from natural clay. Appl Clay Sci 2023;243:107087.
31. Olegario EM, Gili MBZ, Celikin M. Characterization of Philippine natural bentonite. Exp Res 2021;2:e25.
32. Bakalár T, Kaňuchová M, Girová A, *et al*. Characterization of Fe (III) adsorption onto zeolite and bentonite. Int J Environ Res Public Health 2020;17(16):5718.
33. Klinyod S, Yomthong K, Iadrat P, *et al*. Rational design of isolated tetrahedrally coordinated Ti (IV) sites in zeolite frameworks for methyl oleate epoxidation. Chem Asian J:e202400669.
34. Borah D, Nath H, Saikia H. Modification of bentonite clay & its applications: A review. Rev Inorg Chem 2022;42(3):265-282.