Application of activated zeolite to quantitative analysis of Pb liquid sample using commercial laser-induced breakdown spectroscopy (LIBS)

H Suyanto¹, A P Utomo¹, M Manurung², W G Suharta¹ and Windaryoto¹

¹Physics Department, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Badung 80361 Bali, Indonesia
²Chemistry Department, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Badung 80361 Bali, Indonesia

E-mail: hery6@yahoo.com

Abstract. The aim of this research is to figure out an activated zeolite ability to immobilize Pb element in liquid sample. The zeolite was made into powder with size of about 400 µm and was activated by NaOH with different concentrations of 0.5, 1, 1.5 and 2 M. Prior to being analyzed by commercial Laser-Induced Breakdown Spectroscopy (LIBS) technique, 0.05 gram activated zeolite of each concentration were soaked into 10 ml solution containing 100 ppm of Pb and then heated and stirred until become dry powder. The powder was then made into a pellet. After being analyzed by LIBS, activation by 1.0 M NaOH was the optimum condition for zeolite to immobilize Pb in solution. The minimum concentration of Pb in liquid sample which could be immobilized by this method was about 5.86 ppm.

1. Introduction

Zeolite is a very stable solid that is three-dimensional hydrated alumino-silicate crystals constructed by interlinked tetrahedral of alumina and silica (AlO₂-SiO₂) [1]. Because zeolite has porous structure, open structure and being few negatively charged mineral in nature, it can react or accommodate a wide variety of cations, such as alkali or alkaline-Earth: Mg²⁺, K⁺, Na⁺, and other metals plus water molecules trapped in the gaps between them to make charged equilibrium [2]. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Because of these properties, naturally occurring zeolite is widely used in many applications such as adsorbent, electrons transfer media in voltammetry instrument, and others [3-5].

Natural zeolite is not pure alumino-silicate crystals, but it contains organic and inorganic impurities as mentioned above. However, this zeolite can originally conduct exchange between its positively charged ions with other positively charged ions trapped inside them, although in low concentration. Therefore, it is necessary to increase its performance through an activation process [6]. The activation process is used to remove cations and other impurities for increasing surface area and size of zeolite pore as well as reducing Si/Al ratio [6-10]. There are two activation processes, physical activation method by heating process and chemical activation method by dissolving into base or acid solution [6, 11].

This research used natural zeolite from Penggajawa village, Ende district, East Nusa Tenggara Province, Indonesia that was activated by NaOH in different concentration. This kind of zeolite had...
already been applied for adsorbing Pb element and was analyzed by using voltammetry method [4]. Therefore, the aim of this work is to find the optimum condition for activated zeolite to adsorb Pb ion in liquid sample and analyzed by using another method, which is laser-induced breakdown spectroscopy (LIBS).

2. Experimental procedure

2.1. Sample preparation
The zeolite sample used in this study was originated from Penggajawa village, Ende district, East Nusa Tenggara Province, Indonesia. Prior to undergoing activation process, the zeolite sample was grounded into fine powder and sieved to approximately 400 µm in diameter. The zeolite powder was then soaked in demineralized water for 24 hours before cleaning. This step was repeated 3 times. For activation process, the cleaned zeolite powder was soaked in various NaOH concentrations of 0.5, 1.0, 1.5, 2 M and stirred for 2 hours with a constant temperature of 70 °C. After that, the mixture between zeolite powder and NaOH solution was left to stay for 24 hours before being washed with demineralized water to neutralize its pH. Finally, the activated zeolite powder was dried in room temperature before being used as adsorbent.

To make a sample, a 0.05 g of activated zeolite powder was dissolved in 10 ml of solution containing Pb in various concentration of 10, 30, 50, and 100 ppm and each samples stayed for 2.5 hours. This solution was then heated up and stirred until become dry powder. Prior to LIBS analysis, the dry powder sample was made into a pellet. The wavelength used to detect Pb element in this experiment was 405.7 nm (Pb I) since it has 1000 times higher intensity compare to the other wavelengths [12].

2.2. Experimental Setup
The commercial LIBS configuration used in this study is shown in figure 1. The system consists of Nd:YAG laser (CRF 200, λ=1064 nm, 7 ns), Ocean Optics HR 2500+ spectrometer, and AddLIBS software for elemental analysis. For this experiment, the laser was operated at 5 Hz repetition rate with laser energy of 120 mJ. The laser beam was focused through biconvex lens onto the surface of the zeolite pellet and the emission lines from the luminous plasma were captured by a spectrometer containing 14,336 CCD pixels in the wavelength range of 200-900 nm with resolution of 0.1 nm. All experiments were conducted with gate delay of 1 µs, accumulation of 3 shots and at 1 atm pressure of surrounding air.

![Figure 1. Experimental setup [13].](image-url)
3. Results and discussion

3.1. Optimum condition for activation
Zeolite is a kind of stone which is usually available in the sea, abundant and invaluable. It is normally able to immobilize some elements in liquid at low ability. The performance of zeolite can be enhanced by doing chemistry activation method. In this work, the zeolite was activated using 1.0 M NaOH. The activated zeolite was then characterized using LIBS and the result is shown in figure 2. The graph exhibits emission lines intensity of element as a function of wavelength on Pb line region. There is no Pb I 405.7 nm line from both activated and inactivated zeolite. Therefore, this zeolite can be applied to detect Pb element in liquid sample. Due to activation process, the emission intensity of K I 404.4 nm reduced to about one-tenth compared to inactivated zeolite and the presences of other impurity elements were also confirmed except for Na, H and O elements. Increases in porosity and surface area of zeolite will enhance its performance to immobilize element in liquid. Besides, it was also already confirmed that before activation process, the zeolite contained some elements such as Al, Ca, Fe, Ba, K, Na, Si, H, and O.

![Figure 2. Spectra of activated and inactivated zeolite before being soaked in liquid sample containing Pb element.](image)

In order to apply zeolite, 0.05 gr of activated and inactivated zeolite was each dissolved in 10 ml of standard solution containing 100 ppm of Pb and then heated and stirred until it became dry powder. The result of LIBS analysis is shown in the figure 3. A strong enough emission of Pb I 405.7 nm line was detected in activated zeolite and there was a small signal in the inactivated zeolite. K I 404.4 nm and 404.7 nm signals also increased. It can be predicted that the solution contained K element. The appearance of Pb signal and the rising of K signal indicate that the activated zeolite was more energetic to immobilize some elements in the liquid, whether through adsorption, cation exchange or other processes.

To optimize the analytical zeolite performance in term of immobilizing elements in the solution, it is necessary to vary the NaOH activation concentration of 0.5, 1.0, 1.5, and 2.0 M. 0.05 gr of each activated zeolite was dissolved in 10 ml of standard solution containing 100 ppm of Pb and was then heated and stirred until become dry powder. Figure 4 shows the result after being analyzed by LIBS. The average signal intensity of Pb I 405.7 nm rises with increasing NaOH concentration up to 1 M and then drops in the following concentrations. Decreasing emission intensities in higher NaOH
concentration may be caused by broken structure of zeolite and as the result, it did not immobilize Pb element in the solution as much as expected.

![Image of spectra](image-url)

**Figure 3.** Spectra of 1.0 M NaOH activated zeolite and inactivated zeolite after being soaked in liquid sample containing 100 ppm Pb element.

![Image of emission intensity](image-url)

**Figure 4.** Emission intensity of Pb I 405.7 nm as a function of NaOH activation concentration on zeolite.

### 3.2. Quantitative analysis
The analytical performance of activated zeolite can be obtained by lowering the quantity or concentration of Pb in liquid sample so that it would be reliably adsorbed and detected by this method. To confirm this statement, a Pb concentration series of 10, 30, 50, and 100 ppm were used in this work and the result is exhibited in figure 5.

Figure 5 depicts the emission intensity of Pb that increases linearly from 10 ppm to 100 ppm in liquid sample with an equation of $y = 0.3274 \times -1.384$. The limit of detection (LoD) of Pb based on this equation can be calculated to be about 5.86 ppm [14, 15]. This LoD is about three times higher...
compared to that of voltametry method [4]. However, this method is simpler than voltametry and AAS methods in term of sample preparation and detection. In addition, by using this method, some elements in the sample can be analyze simultaneously.

**Figure 5.** Calibration curve for Pb element in the solution.

4. Conclusion
In conclusion, activated zeolite could increase the ability to immobilize Pb element in solution and to transform it into solid phase. This element can be detected by LIBS technique with following conditions: 120 mJ of laser energy, 1 μs delay time detection and an accumulation of 3 shots. 1 M of NaOH was the maximum condition for zeolite activation so that the LIBS system could detect down to 5.86 ppm of Pb in liquid sample.

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