Study of adsorption Ag and Pb in liquid sample using Berea sandstone by commercial laser-induced breakdown spectroscopy (LIBS)

H. Suyanto*, N. Wendri, U. Agustiningrum, M. Manurung

1Physics Dept.,
2Chemistry Dept., Mathematics and Natural Sciences Faculty, Udayana University
Jl. Kampus Bukit Jimbaran-Denpasar- Bali 80361

*Email : hery6@yahoo.com

Abstract. Qualitative and quantitative analysis of Pb and Ag elements in liquid samples had been done by commercial laser-induced breakdown spectroscopy (LIBS) using adsorption method on a Berea Sandstone. The aim of this study is to identify the thickness of the Berea Sandstone for adsorbing Pb and Ag elements in liquid. The experiment was started with characterizing the Berea Sandstone that contains Si, Na, H, Li, K, Ca, O, N, Be, Ti, Al, Mg and Ba. Some of these elements have ability to adsorb Pb and Ag elements in the liquid. To prove this phenomenon, it is required to look for the experiment parameter optimum conditions such as laser energy, adsorption time and sample temperature. The experiment was conducted by dropping 2 ml standard liquid containing 1000 ppm of Pb and Ag to the Berea Sandstone surface. The result showed that the parameter optimum conditions for analyzing Pb and Ag elements in liquid sample with adsorption method were adsorption delay-time of 15 minutes, laser energy of 120 mJ and sample heating of 80 °C. The next experiment was focused on the number of adsorption as a function of depth. The data showed that Pb and Ag elements in liquid sample of 2 ml, 1000 ppm were fully adsorbed by the Berea Sandstone until the depth of 0.372 mm and 10.40 mm from the surface, respectively. The data also showed that the limit of detection predicted to about 22.76 ppm.

1. Introduction
Berea Sandstone is a sedimentary rock whose grains are predominantly sand-sized and are composed a lot of quartz (± 93%) held together by silica [1]. The relatively high porosity and permeability of Berea Sandstone makes it a good reservoir rock. Berea Sandstone from Bonbiu village, Gianyar city, Bali Province, Indonesia used in this study has special performance. People in this village usually make the Berea Sandstone a special shape like bowl called Topo used to filter groundwater before drinking or another uses. People usually just see the water after filtering cleaner and used it, but they do not know whether Topo can filter some hazard elements such as Pb and Ag elements as water pollutant or not. Therefore, this work analyzes the ability of Berea Sandstone as a water-filter using laser-induced breakdown spectroscopy (LIBS) through adsorption method.
Laser-induced breakdown spectroscopy (LIBS) has been employed in a variety of analytical applications and maintained its constant growth since its introduction in the early eighties [2]. The spectral analysis of the emission lines from the plasma provides the elemental compositions of the target. Therefore, LIBS has many advantages both either qualitative or quantitative analysis with very fast and accurate to gas and solid samples, but not in liquid sample. Liquid sample will splash off when laser beam is focused on liquid sample surface and it does not produce plasma. To anticipate this condition, many researchers worked special methods. One method, analyzed Al<sup>3+</sup> in solution until 1.5 ppm using droplet method which change liquid phase to gas phase and others, analyzed liquid sample using deposition method which used filter-paper and electrical deposition to aluminum surface [3-7].

Finally, there are two goals of this work, first is to looking for the minimum thickness of the Berea Sandstone to filter or adsorb Pb and Ag elements in liquid samples. Secondly, to determine minimum Pb concentration adsorbed by the Berea Sandstone. All analysis used Laser-Induced Breakdown Spectroscopy (LIBS).

2. Experimental Procedures

2.1. Sample Preparation

The research was conducted in 2 steps that are to determine optimum conditions of parameter (such as delay time reaction, sample temperature, laser energy) and quantitative analysis. For the first step, 2 ml liquid sample containing 1,000 ppm of Pb was dropped onto the surface of Berea Sandstone and time lag treatment of 1, 5, 15, 25, 35 and 35 minutes before laser irradiation of 60 mJ, 80 mJ, 100 mJ and 120 mJ which was chosen in order to find the best adsorption time. The next treatment, by varying the sample heating temperature of 50, 60, 70, 80, 90 °C after certain time of optimum absorption process in the first treatment.

The second step is quantitative analysis that determine the thickness of the Berea Sandstone for adsorbing Pb and Ag elements in liquid sample and also to determine the minimum concentration (or limit of detection) of Pb element in liquid sample adsorbed by the Berea Sandstone. For this experiment, 3.5 ml liquid sample containing 1,000 ppm of Pb and Ag was dropped onto surface of 0.5 cm and 2.5 cm Berea Sandstone until penetration to another surface. Based on optimized parameter conditions in the first step, the Sandstone was irradiated by laser in the fixed position for four times with accumulation of 4 to get depth profile data [8]. For providing limit of detection data, a 3.8 ml solution containing 50 ppm, 100 ppm, 200 ppm and 400 ppm of Pb were poured to the Berea sandstone surface and analyzed by LIBS.

2.2. Experimental Set-up

The experimental set-up used in this work is presented in figure 1. The commercial LIBS system consists of Neodymium:Yttrium Aluminum Garnet (Nd:YAG) laser (1,064 nm, 7 ns), OOI LIBS and AddLIBS software and Ocean Optics HR 2500+ spectrometer. For this study, the laser was operated at 10 Hz repetition rate with laser energy of 120 mJ. The laser beam was focused through 10 cm focal length biconvex lens onto the Berea Sandstone surface and the resulted emission radiation was captured by optical multichannel analyzer containing 14,336 CCD pixels in the wavelength region of 200 – 900 nm with resolution of 0.1 nm. All the experiments were conducted in surrounding gas of air at 1 atm pressure.
3. Results and Discussion

3.1. Determining of experiment optimum conditions

The first step in this work is to identify the optimum conditions of experiment such as delay time adsorption (or reaction) between solution and Berea Sandstone sample, the temperature of sample and laser energy. Prior to irradiation by laser, the Berea Sandstone sample was dropped 2 ml of solution containing 1000 ppm of Pb. The sample, than, analyzed every 10 minutes with focusing laser of 120 mJ on surface of sample which produced plasma and emission intensity of neutral atomic emission Pb I 405.7 nm [9] captured by spectrometer. It is displayed on figure 2.

Figure 2 show that, the atomic emission intensity of Pb increases with increasing adsorption time from 5th to 15th minute than remains constant till 45th minute. This rising is predicted as interaction between ionic Pb in the solution with some elements of the Berea Sandstone sample through ionic immobility (adsorption) process whether as ionic exchange, complexion or electrons covalence. Therefore, all analysis data in this experiment was conducted 15 minutes after dropping liquid sample on the Berea Sandstone surface.

To explain ionic immobility process, first, the Berea Sandstone sample was qualitative analyzed using LIBS. It contains of Si, Na, H, K, Ca, O, N, Ti, Al, Mg, Fe, Ba elements and there are no Pb and Ag elements. Based on this data, it can be predicted that ionic immobility process between ionic Pb and the Berea Sandstone sample through ionic exchange process, where element such as Ca will be replaced by ionic Pb as it has similar radius to ionic Pb. Another possibility, the SiO₂ molecule in the sample has free electrons and these electrons will be used together with ionic Pb produced electron covalence process. However, all these ionic immobility processes must be investigated futher.

After obtaining the experiment optimum conditions of delay time absorption, the next step is to know the influence of sample temperature and laser energy to emission intensity of Pb line. After dropping 2 ml solution containing 1000 ppm of Pb, the Berea Sandstone samples were varied its temperature from 50 C to 90 C and were analyzed using varied laser energy from 60 mJ till 140 mJ. Results are exhibited on figure 3.

Figure 3, displays that the neutral atomic emission intensity of Pb I 405.7 nm increases with increasing laser energy till 140 mJ as well as increasing temperature of sample till 80 C. More laser energy applied, Pb atoms propelled with higher speed and adiabatic compression take placed with surrounding air that produce shockwave with higher energy. This energy is absorbed by Pb electrons for exciting to higher level energy, than emit photon of certain wavelength when it experiences transition to ground state. Because of higher energy of shockwave, a lot of Pb atoms excited and as a
consequence higher emission intensity produced. However, because of a lot of dust produced when 140 mJ of laser energy focused on surface sample, therefore these all experiment used 120 mJ.

In the case of sample temperature, increasing temperature will increase intermolecular bonds between particles and as a result the recoil force rises when laser focused on it. Increasing recoil force, the Pb atoms propelled with higher speed and the same results as increasing laser energy. On the other hand, when the temperature was increased to 90 °C, the emission intensity of Pb I 405.7 nm decreased. It might be caused by the break up intermolecular bonds in the sample and as a consequence the recoil force decreased when laser focused on it. Therefore, the experiment optimum parameters used in this work (delay time absorption, sample temperature and laser energy) were 15 minutes, 80 °C and 120 mJ, respectively.

3.2 Depth Profile Analysis

Based on the experiment optimum conditions, the next experiment was focused on quantitative analysis concerned on an ability of the Berea Sandstone sample to adsorb ionic Pb element in solution till certain depth on sample called depth profile analysis. The Berea Sandstone sample 0.5 cm thick was dropped 2 ml solution containing 1000 ppm of Pb and waiting till penetrated to another side. Using the experiment optimum conditions, the sample was analyzed every 4 shots until 20 shots laser from surface or front side and then it was analyzed from another side (back side). The results displayed on figure 4. The number of shots stoped on 20 shots to avoid the confinement effect [10].

Figure 4 shows that the emission intensity spectrum of neutral Pb line decreases slowly with increasing the depth or the number of laser shots. It means the Pb element adsorbed or filtered gradually by sample from the surface. On the other hand, when it was analyzed on the other surface (back side), there was no emission intensity of Pb line. To identify the depth of Pb element filtered by sample, it is better to do linear regression process between the emission intensity as a function of laser shots. Based on data figure 4 obtained y = - 0.825 x + 56.9. From this equation, the Pb element adsorbed by sample is about 73 laser shots or equivalent to about 0.372 mm from sample surface. This result agrees with figure 4 that there is no signal after 5 mm in depth.
To know the ability of the Berea Sandstone sample to immobilize another element in the solution, dropped 2 ml solution containing 1000 ppm of Ag and waiting till penetrated to another side of 5 mm thickness. The same procedure as analyzing of Pb, the depth profile was conducted to detect Ag element as a function of the laser shots. The result is displayed on figure 5.

Figure 5 exhibits the emission intensity of neutral atom of Ag I 328.06 nm that degrades with the number of laser shots, however, the intensity rises again when it was analyzed from another side (back side). To know the depth of Ag element filtered by Sandstone, it is better to do linear regression process between the emission intensity as a function of laser shots as Pb case. Based on data figure 5, the linear regression equation is $y = -0.0052x + 54.592$, that is correlation to the Ag element adsorbed by the Berea Sandstone to about 1.05 cm from sample surface. This result agrees with the figure 5 that there is significant signal after 0.5 cm in depth.
To use the Berea sandstone for filtering the Ag element in liquid sample, the thickness of Berea sandstone is at least 1.05 cm. To prove this statement, the 3.8 ml containing 1000 ppm of Ag element was dropped until it penetrates to the Berea sandstone with thickness of 2.5 cm. The same procedure as before and after analyzing with LIBS, the emission intensity of Ag displayed on figure 6. Figure 6 shows that emission intensity on the back side or 2.5 cm from surface is zero. It means that the Ag element in solution did not penetrate after 2.5 cm from surface.

The immobility phenomenon of Ag element which is adsorbed by Berea sandstone can be described as follow. The ion Ag⁺ in solution combines with ammonia molecule in the Berea sandstone to produce a co-ordinate bond [Ag(NH₃)₂]⁺ which N provides both the electrons for a covalent bond. In this case ion Ag⁺ and N act as electron acceptor and electron donor, respectively [11].

3.3. Quantitative Analysis

Quantitative analysis in this study is to know the minimum Pb element in the solution which can be adsorbed by the Berea Sandstone. Therefore, a 2 ml solution containing 50 ppm, 100 ppm, 200 ppm and 400 ppm were poured to the Berea Sandstone surface. After analyzed by LIBS, the emission intensity of Pb of each concentrations were plotted as shown in figure 7.
Figure 7, states that the emission intensity of Pb decreases linearly from 400 ppm to 50 ppm with an equation \( y = 0.0966x + 1.5826 \). The limit of detection (LOD) of Pb can be calculated by using equation \( y = \frac{CL}{sd} \), where CL, sd, and m are limit of detection (LOD), standard deviation and a slope of calibration curve respectively [2,12]. Based on data in figure 7, the LOD of Pb is 22.76 ppm.

In conclusion, the Berea sandstone has the ability to adsorb Pb and Ag elements in solution and transform to solid phase. These elements can be detected by LIBS technique with some conditions such as delay time adsorption, the sample temperature and laser energy were 15 minutes, 80°C and 120 mJ respectively. This Berea Sandstone can filter or adsorb 1000 ppm of Pb and Ag elements in solution until the depth of 0.372 mm and 10.49 mm respectively. Besides, the Berea Sandstone also has the ability to filter Pb element in solution to about 22.76 ppm.

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