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Citation: *AIP Conf. Proc.* **1555**, 32 (2013); doi: 10.1063/1.4820987

View online: <http://dx.doi.org/10.1063/1.4820987>

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Study of Filtering Ag Liquid Sample by Chitosan Biomembrane Using Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract. The capability of Laser-Induced Breakdown Spectroscopy (LIBS) to resolve filtration process of Ag liquid sample by chitosan biomembrane is demonstrated. The biomembrane was prepared by inversion method used to filter Ag liquid using pressurized technique samples which were then analyzed by monitoring the emission corresponding to Ag (I) at wavelength of 328 nm. The experiment was conducted by varying the laser energy i.e. 80, 120, and 160 mJ, where, subsequently, and its effect on the depth-profile from 20 - 200 μm was characterized by LIBS. The results showed that the physical processes of pressurized filtration led a homogeneous Ag in the membrane from the surface to a depth of 200 μm . The optimum condition was obtained at laser energy of 120 mJ. The adsorption occurred only on the surface of the membrane i.e. 20 μm depth, but there was no inclusion. Improvement of the detection performance of adsorption process was done by heating the dripped membrane at 35 °C and was resulting in increase in emission intensity as expected.

Keywords: Chitosan biomembrane; pressurized filtration; liquid Ag; Laser-Induced Breakdown Spectroscopy

PACS: 82.35Pq

INTRODUCTION

Chitosan is the most abundant natural polymer after cellulose. It is a partially deacetylated product of chitin, which has many useful features such as non-toxic, biocompatibility, biodegradability, and antibacterial property. Due to its features, chitosan has been widely applied in many industries including wastewater treatment. Chitosan has the ability to form complexes with metals. It exhibits higher adsorption capacity for metal ion compared to that of chitin owing to the amino group content. However, the serious drawback of chitosan for metal ion adsorbent from practical utilization is that it is soluble in acidic media [1-2].

Laser induced breakdown spectroscopy (LIBS) or laser induced plasma spectroscopy is a useful method to determine the chemical composition of a wide range of materials including metals, liquids, aerosols, plastics, minerals, biological tissues, etc. [3]. As an analytical technique, LIBS presents some advantages to other techniques: no sample preparation, real time analysis, contactless analysis, apparatus or experimental simplicity, inexpensiveness, robustness, and quickness are interesting properties which makes LIBS an attractive analytical technique. In many cases is a non destructive technique [1]. In this technique

one requires a pulsed laser for generating micro-plasma on the target surface and elemental analysis is accomplished by studying the emission of the plasma plume. The performance of LIBS depends on several parameters including laser wavelength, pulse energy, pulse duration, time interval of observation, and geometrical configuration of collecting optics, target features, and properties of ambient medium. Extensive work has been devoted to optimize these parameters for the best experimental and commercial realization of this technique.

The main disadvantage of LIBS is the high limit of detection, about 500 ppm but 1ppm can be reached for some elements [4].

LIBS is a very versatile technique and have been used in siderurgy, industrial process control [4-7], environmental geochemistry, biohazard material detection, forensic science, microbiology, odontology, archaeology, cultural heritage and art conservation [8-12].

Several papers dealing with LIBS applications in depth-resolved analysis have also reported [5, 9-13]. In their reports, the laser was focused to a different extent resulting in high irradiances (typically in the order of 10⁹ - 10¹¹ Wcm⁻²).

In this study, the main purpose is to explore the capability of Laser-Induced Breakdown Spectroscopy

International Conference on Theoretical and Applied Physics (ICTAP 2012)

AIP Conf. Proc. 1555, 32-35 (2013); doi: 10.1063/1.4820987

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(LIBS) to resolve filtration process of Ag liquid sample by chitosan biomembrane using pressurized technique. Depth profile analysis was conducted by varying laser energy from 80 to 160 mJ each for 20 to 200 μm depth. Various methods of the adsorption process of Ag solution in the membranes were also carried out i.e. control (without treatment) is called as Sample-1; natural adsorption as Sample-2; adsorption by heating as Sample-3; adsorption after heating as Sample-4; and adsorption with pressure as Sample-5.

MATERIALS AND METHODS

a. Materials

The materials used are Chitosan powder with characteristics i.e. 87,9% deacetylated and their solubility in acetic acid is 99,4%; acetic acid and sodium hydroxide p.a. All reagents were analytical grade and were used without further purification.

b. Preparation of Chitosan Membrane

The chitosan solution of 4% (w/v) was prepared by dissolving 10 g of chitosan powder in 250 ml of 1% acetic acid solution. The mixture was stirred for 8 hours at room temperature to obtain dope solution. The dope solution was poured into a glass plate and dried at room temperature for 6 days. The membrane was in the NH_3^+ form. It was dipped in 1% sodium hydroxide solution to reach the uncharged amino form, washed with distilled water 3 times to eliminate the excess of sodium hydroxide, then dried. The thickness of the membrane was around 236 μm .

c. Membrane Treatments

In this study, the chitosan biomembranes have been treated in 5 different ways i.e. Sample-1: control (without treatment), Sample-2: Ag 1000 ppm dropped on the membrane and allow to dry naturally (natural adsorption), Sample-3: Ag 1000 ppm dropped on the membrane and heated to 35°C (adsorption by heating), Sample-4: heat the membrane to 35°C then dropped with Ag 1000 ppm (adsorption after heating), and Sample-5: membrane exposed to Ag 1000 ppm solution by filtration method with pressure ~ 50 kPa (adsorption with pressure).

d. Laser-Induced Breakdown Spectroscopy (LIBS)

Laser induced breakdown spectroscopy was used to probe the present of Ag element in the pressurized treated chitosan biomembrane at various depths from the surface. The LIBS 2500-7 plus model was used. It uses Nd-YAG Laser (1064 nm (wavelength), 7 ns (pulse width), 200 mJ (max. energy)) and *echelle* HR 2500 spectrometer with specifications such as, range of the spectrum 200-980 nm, with 7 channels, FWHM resolution of 0,1 nm using 7 detectors with 2048 *element linier silicon CCD arrays* that given total of 14336 pixels. The output of the spectrometer analyzed by *OOLIBS* and *OOICOR* softwares that displayed on the monitor.

In the present study, the delay time used was 1 μs , 4 pulses of each scan, and 0 pulse cleaning (to avoid unnecessary scan). The laser energy density (fluence) employed in the experiments was in the range 60-180 mJ. The pulse to pulse energy variation throughout all measurements performed, was no $> \pm 5\%$. The sample was placed approximately 2 cm in front of the focal point and a relatively wide spot (approx. 1 mm) was used in the LIBS measurement in order to obtain a representative average of the material composition. Emission spectra were recorded separately for each one of successive laser pulses and were subsequently analyzed.

RESULTS AND DISCUSSION

Figure 1 shows LIBS spectra of control (Sample-1) and pressurized treated chitosan biomembrane (Sample-5) scanned with laser energy of 120 mJ in the range 327 - 329 nm. It shows a peak at wavelength of 328 nm in Sample-5 which is known as atomic emission line of Ag (I), whereas no peak observes in the control membrane (Sample-1). This explains that there is Ag in the Sample-5 that admitted by pressure.

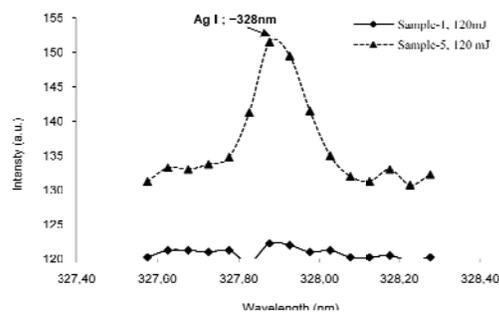


FIGURE 1. LIBS spectra of control (Sample-1) and pressurized treated chitosan biomembrane (Sample-5) scanned with laser energy of 120 mJ in the range 327 - 329 nm.

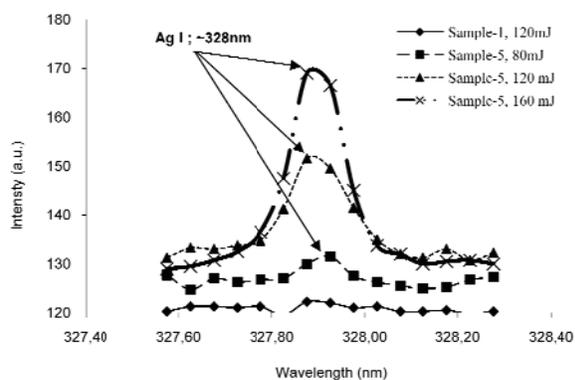


FIGURE 2. LIBS spectra of the pressurized chitosan biomembrane (Sample-5) in the range 327 - 329 nm for laser energies 80, 120, and 160 mJ. Control (Sample-1) spectrum is presented (kept at laser energy of 120 mJ) for the comparison.

Figure 2 shows LIBS spectra of the pressurized chitosan biomembrane (Sample-5) in the range 327 - 329 nm for varies of laser energies 80 mJ, 120 mJ, and 160 mJ. Control (Sample-1) spectrum at laser energy of 120 mJ was also kept for the comparison. It shows that the intensity of Ag (I) peak increases with increasing laser energy. This describes more number of electrons from the atoms and more ions have been excited hence more emission of spectrum obtained. The spectrum also shows increasing in the background signal as laser energy increases, which is due to the continuum emission of the plasma form [14]. From these results, further experiments were focused and analyzed on laser energy of 120 mJ and stated as optimal condition for the chitosan biomembrane.

Figure 3 shows the intensity of atomic emission of Ag (I) at wavelength of 328 nm obtained by LIBS (with laser energies 80, 120, and 160 mJ) as a function of depth from the surface, of the pressurized chitosan biomembrane (Sample-5). The graph shows that the emission was observed for all depths indicating that Ag has been evenly distributed within the sample. At the higher laser energy, 160 mJ shows fluctuation. This means that the intensity of the background increase, the peak becomes broad and self adsorption process take place.

For further examination of Fig. 3, the standard deviation of the LIBS intensity was calculated by measuring the intensity from three identical series of adjacent areas on the sample surface. The overall standard deviation in the intensities of Ag (I) was ~ 2% for laser energy 80 and 120 mJ, and ~ 5% for 160 mJ.

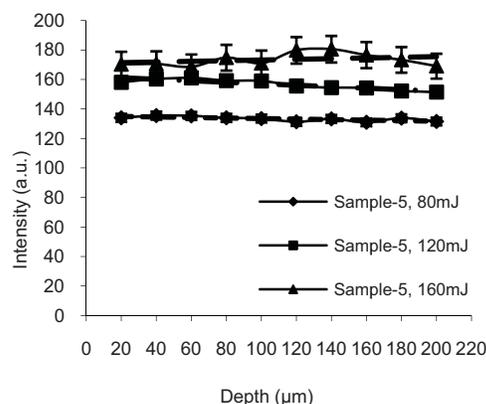


FIGURE 3. Intensity of atomic emission of Ag (I) at wavelength of 328 nm obtained by LIBS with laser energies 80, 120, and 160 mJ as a variation of depth from the surface for the pressurized chitosan biomembrane (Sample-5).

To study about the adsorption process of Ag in the chitosan biomembrane, four methods membrane treatment are introduced. The results are shown in Fig. 4. For natural (Sample-2) after first shot (shot-1, depth ~ 20 μm) by laser energy of 120 mJ, the intensity of Ag (I) obtained was ~ 6.67 a.u., while at a depth of 40 μm (second shot) was null, indicating that no inclusion process occurred. To improve the detection performance of the adsorption processes, an adsorption by heating method was introduced, the treated membrane with the same process of Sample-2 is heated to 35°C (Sample-3) and the intensity is increased to ~ 8.75 a.u. This indicates that the process was influenced by the temperature. Result from the second shot was also zero. Furthermore an adsorption after heating method was used. Heating the membrane before dripping it with 1000 ppm Ag solution (Sample-4), gave intensity as low as, ~ 5.5 a.u. The intensity of Sample-5 (adsorption with pressure method) was the highest at ~ 21.5 a.u.

These results describe Ag liquid penetrate into the membrane properly when pressurized (adsorption with pressure method). This causes Ag interact both chemically and physically with the membrane and produces strong covalent bonds in the membrane. As a result, providing a strong rebound momentum during the laser shot and produced plasma emission intensity Ag (I) at wavelength of 328 nm is high compared with other adsorption methods.

ACKNOWLEDGMENTS

The authors wish to thank the Faculty of Mathematics and Natural Sciences, Udayana University for the LIBS facility.

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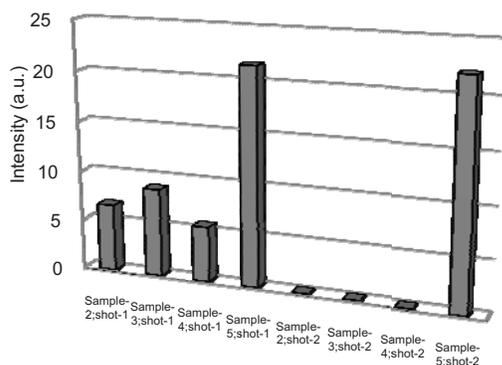


FIGURE 4. Intensity of emission of Ag (I) at wavelength of 328 nm for various membrane treatments.

The adsorption processes occurred in the chitosan biomembrane can be described as follows. The Ag^+ ions which were chemically adsorbed through bonding with N in $[\text{Ag}(\text{NH}_3)_2]^+$ as a covalent bond resulted in only a pair of electrons shared by atoms N. Such a bond is called a coordination covalent bond. Here, Ag^+ ion is an electron acceptor, while N is an electron donor. Therefore, the formed adsorption layer is not sufficiently strong when the laser shot and hence gave relatively low emission (Sample-2). To enhance the results of this adsorption, the reinforcement was carried out by heating (Sample-3) and produce relatively higher emissions than without heating (Sample-2). The adsorption after heating method produced low emissions. In this case, heating had caused a damage to the physical structure of the membrane and eliminating or reducing the number of N that acted as Ag adsorption media, thus resulting in a low intensity.

CONCLUSION

The present study demonstrated laser induced breakdown spectroscopy (LIBS) to probe the present of Ag element in the pressurized treated chitosan biomembrane at various depths from the surface. It was analyzed by monitoring the emission of Ag I (wavelength of 328 nm). The pressurized filtration process resulted in a homogenously distributed Ag in the membrane up to a depth of 200 μm . The optimum laser energy was 120 mJ. The chemical adsorption process occurred only at the surface of the membrane without inclusion. Improvements can be done by heat treatment at 35°C.