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EVALUATION OF THE FUNCTIONALIZATION OF GOLD NANOPARTICLES PREPARED BY LASER ABLATION FOR THE DETECTION OF HEAVY METALS IN POLLUTED WATER SAMPLES

EVALUACIÓN DE LA FUNCIONALIZACIÓN DE NANOPARTÍCULAS DE ORO PREPARADAS POR ABLACIÓN LÁSER PARA LA DETECCIÓN DE METALES PESADOS EN MUESTRAS DE AGUA CONTAMINADA

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ABSTRACT

The research was carried out with the purpose of functionalizing AuNPs gold nanoparticles prepared by laser ablation for the detection of heavy metals in contaminated water samples in the province of Tayacaja Huancavelica. The solid state pulsed Nd: YAG laser was used to produce gold nanoparticles by the laser ablation technique, using as a target a 24 carat gold plate with dimensions 1 cm x 1 cm with a thickness of 1mm, immersed in 20 ml of ultrapure water contained in quartz cuvettes. The nanoparticles were characterized by UV-Vis spectrophotometry. The target was ablated with infrared radiation of wavelength at 1064 nm from the laser equipment, with energy of 60.28 mJ/p and 32.99 mJ/p at a frequency of 10 Hz, for 60 minutes. AuNPs were obtained in colloidal state, whose diameters were 25 nm calculated with the spectrophotometer, observing an absorption peak centered at 518.12 nm characteristic of spherical gold nanoparticles. It is concluded that AuNPs in colloidal state allow the detection of heavy metals the concentrations of lead, cadmium and arsenic contained in water, by changing the color of the AuNPs colloid proportional to the concentration of each heavy metal detected. It is concluded that AuNPs in colloidal state allow the detection of heavy metals the concentrations of lead, cadmium and arsenic contained in water, by changing the color of the AuNPs colloid proportional to the concentration of each heavy metal detected. It is concluded that AuNPs in colloidal state allow the detection of heavy metals Cd2+, Pb2+, and As+2 in water.

Keywords: Laser ablation, colloidal, gold nanoparticles, spectrophotometry, heavy metals, L-cysteine.

RESUMEN

La investigación se realizó con el propósito de funcionalizar nanopartículas de oro AuNPs preparadas por ablación láser para la detección de metales pesados en muestras de agua contaminada en la provincia de Tayacaja Huancavelica. Se utilizó el láser Nd:YAG pulsado de estado sólido para producir nanopartículas de oro mediante la técnica de ablación láser, utilizando como blanco una placa de oro de 24 kilates de dimensiones 1 cm x 1 cm con un espesor de 1 mm, sumergida en 20 ml de agua ultrapura contenida en cubetas de cuarzo. Las nanopartículas se caracterizaron por espectrofotometría UV-Vis. El objetivo fue ablacionado con radiación infrarroja de longitud de onda a 1064 nm del equipo láser, con energía de 60,28 mJ/py 32,99 mJ/pa una frecuencia de 10 Hz, durante 60 minutos. Las AuNPs se obtuvieron en estado coloidal, cuyos diámetros fueron de 25 nm calculados con el espectrofotómetro, observándose un pico de absorción centrado en 518,12 nm característico de las nanopartículas esféricas de oro. Se concluye que las AuNPs en estado coloidal permiten la detección de metales pesados las concentraciones de plomo, cadmio y arsénico contenidas en el agua, al cambiar el color del coloide de las AuNPs proporcional a la concentración de cada metal pesado detectado. Se concluye que las AuNPs en estado coloidal permiten la detección de metales pesados las concentraciones de plomo, cadmio y arsénico contenidas en el agua, al cambiar el color del coloide de las AuNPs proporcional a la concentración de cada metal pesado detectado. Se concluye que las AuNP en estado coloidal permiten la detección de metales pesados Cd2+, Pb2+ y As+2 en agua.

Palabras clave: Ablación láser, coloidal, nanopartículas de oro, espectrofotometría, metales pesados, L-cisteína.

INTRODUCTION

Nanoscience is the discipline dedicated to the study of the properties of materials with dimensions of the order of nanometers (Soriano, et al., 2018). Nanotechnology comprises the study, synthesis and application of materials through the control of matter at the nanoscale.

Nanomaterials constitute an important branch in the growing field of nanoscience. The reduction in size can lead to a whole host of new physicochemical properties and a host of potential applications (Kaphle, et al., 2018). Nanomaterials are defined as materials with a length less than 100 nm in any of their dimensions. This characteristic gives them properties and behaviors different from those exhibited by the same solid material in bulk and with the same composition (De Mello Donegá, 2014). So, Chen the size of a material is continuously reduced, from macroscopic dimensions to the smallest, initially the properties remain the same and then slight changes begin to appear; finally, when the size falls below 100 nm, abrupt variations in its properties appear. If one dimension is reduced to a nanometric order, while the other two dimensions remain large, we obtain the structure known as a quantum well (Bajorowicz, et al., 2018). If two dimensions are reduced, while the third remains large, the resulting structure is called a quantum wire. The extreme case of this size reduction process, in which all three dimensions become nanometric, is known as the quantum dot (Moon, et al., 2019).

The optical properties of metallic nanoparticles, including Au, have been used since ancient times, such as the Lycurgus cup (Schaming & Remita, 2015; Alberti, et al., 2021); containing gold nanoparticles embedded in glass presenting el green color when the light source strikes frontally with the cup and ruby color when lit from behind (Freestone, et al., 2007). Experimentation with nanostructures began approximately 100 years ago, after Faraday carried out the first experiment in which he synthesized pure gold colloids by chemical reduction of a gold chloride solution.

Nanostructures have at least one dimension in the range of 1 to 100 nm, these are differentiated by sizes at the nanoscale: nanoclusters are structures that have 1 to 100 nm in each spatial dimension, they are classified as 0D nanostructures. Nanotubes, nanorods and nanowires also have a characteristic diameter between 1 and 100 nm and a length that could be much greater, they are classified as 1D nanostructures. Likewise, the nanotextured surfaces or thin films have a thickness between 1 and 100 nm, while the other two dimensions are much greater; These structures are classified as 2D nanostructures and have many applications as nanosensors (Wahab, et al., 2019).

Fabrication of nanoscale structures or devices is achieved using a bottom-up or top-down approach. Bottom-up approaches seek to have smaller components integrated into more complex assemblies, while top-down approaches seek to create nanoscale devices by using larger externally controlled devices to drive their assembly (Isaacoff & Brown, 2017). The chemical method is associated with the bottom-up approach and the physical with top-down (Yu, et al., 2021). In this research, the top-dow approach was used, generating the nanoparticles from a metallic gold sample of dimensions 1cm x 1cm with a thickness of 1 mm. Laser ablation was applied with a frequency of 10 Hz at different powers in the range of 50 to 60 mJ/p and with a duration of 30 to 60 min, achieving spherical nanoparticles of approximately 20 nm in diameter.

Gold nanoparticles are characterized by having a wavelength and surface plasmon resonance (SPR) in the visible region, which makes it possible to determine the shape and size of the nanoparticles and the optical dispersion in the medium that surrounds them (Freitas de Freitas, et al., 2018). Metals such as Au, Ag, Cu and the alkali metals are characterized by an SPR in the visible region of the electromagnetic spectrum. In contrast, transition metals are generally characterized by an SPR in the ultraviolet (UV).

Therefore, the present study aimed to establish a simple and fast colorimetric method for heavy metals in water samples using gold nanoparticles functionalized with L-cysteine as a sensor based on the aggregation of gold nanoparticles, induced by the interaction between Cd^{2+} and L-cysteine, which resulted in the formation of a new ultraviolet absorption peak visible at 600 nm and a color change of the system from yellow-orange to green. The Cd^{2+} in water samples was detected by UV spectrophotometry, being also visible to the eye presenting a purple color. In particular, this study has the potential to provide a real-time monitoring method for the different heavy metals (Cd^{2+}, Pb^{2+}, and As^{2+}) in water samples.

MATERIALS AND METHODS

For the production of the nanoparticles by ablation, the laser equipment of 450 mJ/p power was used, with repetition rates of 10 and 20 Hz, the energy of 450 mJ generates wavelength of 1064 nm, 220 mJ generates wavelength 532 nm, 130 mJ generates 355 nm wavelength, 60 mJ generates 266 nm wavelength, and 10 mJ generates 213 nm wavelength (Quantel, 2019). Pulse duration for all cases was 6 ns, with beam divergence of <0.5 mrad. The control of the production of the nanoparticles was carried out from the touch panel (Figure 1).

Figure 1. High power 450 mJ/p laser equipment for the production of AuNPS by laser ablation.

This type of nanoparticle production corresponds to the physical route where the top-dow approach was used, where the AuNPs were generated by incident laser ablation on a metal plate. The diagram of this approach is presented in Figure 2.

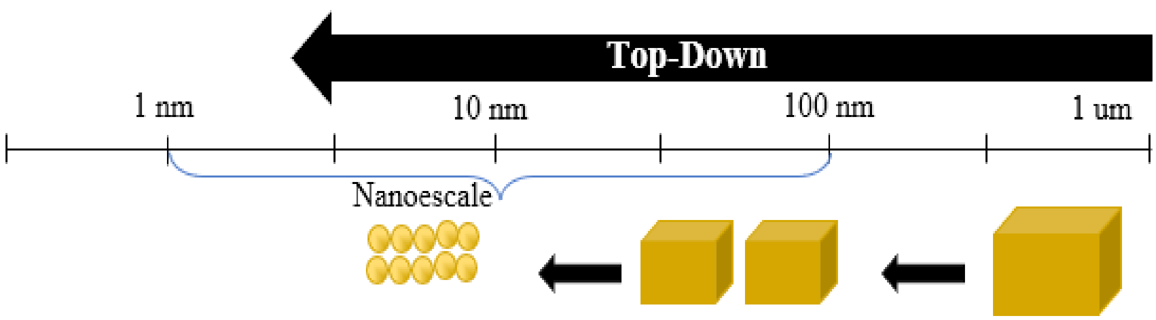

Figure 2. Top-down approach to gold nanoparticle production.

The characterization of the nanoparticles was carried out using the Avantes UV-Visible-IR spectrophotometer with a wavelength of 200 nm to 1,160 nm, with a deuterium-halogen light source AvaLight-DH-S with a length range of 200-1700 nm wave. The spectrophotometer incorporates the 2048x64 detector, which covers applications in the UV and IR range, includes a classification filter to reduce second order effects and purge ports for deep UV measurements. It is configured with FC / PC fiber optic input connectors, uses USB connection for PC, delivering a scan every 2 milliseconds coupled to AvaSoft software(Avantes, 2018), Figure 3 presents the characterization diagram of the AuNPs in colloidal state.

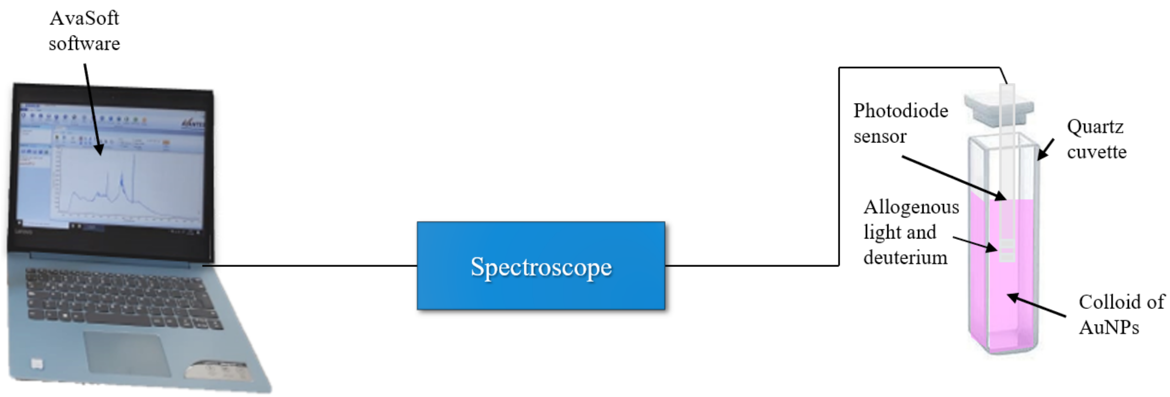

Figure 3. Characterization diagram of AuNPs in colloidal state.

The functionalization of the gold nanoparticles in a colloidal state with L-cysteine ≥ 97% purchased from Sigma Aldrich, was carried out at the same instant of laser ablation on a metallic gold sample of purity ≥ 99.99%. The laser was ablated with wavelengths of 1064 nm for 30 and 60 minutes, as well as by the 532 nm laser for 30 and 60 minutes (Figure 4).

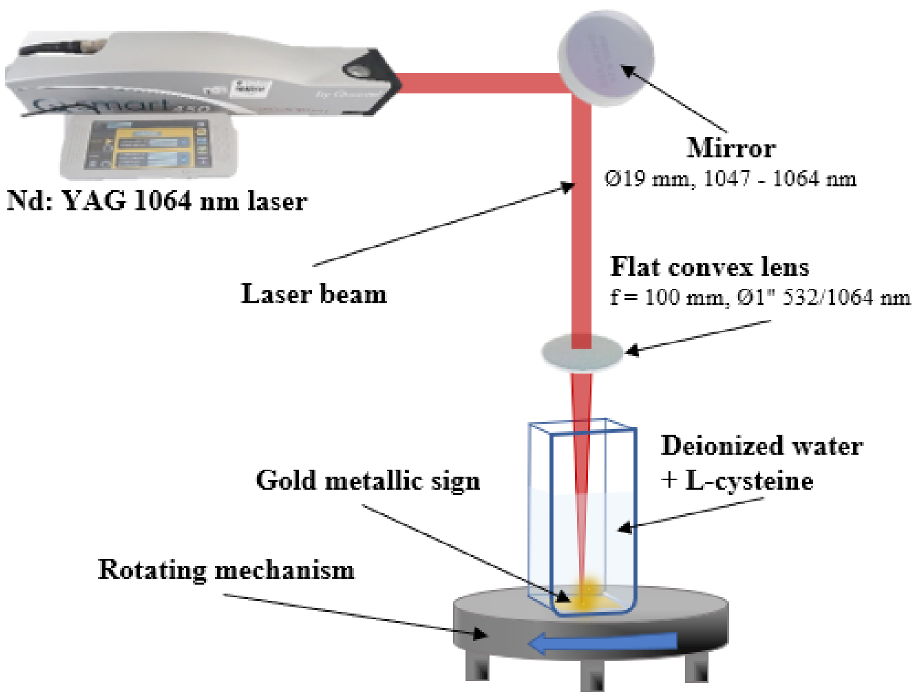

Figure 4. Functionalization of gold nanoparticles with L-cysteine.

The mathematical equation that allowed to theoretically determine the diameter in nm of the nanoparticles, is described by the relation of the absorbance and the concentration of the AuNPs (Haiss, et al., 2007). This relationship is presented in equation 1.

$$d = \frac{\ln\left(\frac{\lambda_{spr}-\lambda_0}{L_1}\right)}{L_2} \quad (1)$$

Having as adjustment parameters: nm, and, while the relationship that allows the concentration to be calculated is given by the diameter and concentration of equation 2, .

$$d = \left(\frac{A_{spr}(5.89 * 10^{-6})}{c_{Au}\exp\left(C_1\right)}\right)^{1/C_2} \quad (2)$$

Where: is the absorbance value at the peak position of the plasmonic resonance, d is the diameter of the AuNPs and is the estimated concentration in particles/cm^3, while the experimental values are and (Haiss, et al., 2007).

For the detection of heavy metals in water, Sigma-Aldrich chemicals were used: cadmium nitrate tetrahydrate with chemical formula $Cd(NO_3)_2 * 4H_2O$ with purity 98%, lead nitrate with formula $Pb(NO_3)_2$ with molecular weight 331.21 with 99.999% purity, arsenic oxide of formula As_2O_3 with trace base metals of 99.995% . These products were used in the experiments without any modification.

RESULTS AND DISCUSSION

The AuNPs in colloidal state were obtained by the pulsed laser ablation technique, using the YAG: 450 laser equipment, for different energy levels and ablation times. For the parameters: delay 110 μs than equivalent in energy of 64.04 mJ/p, wavelength 1064 nm, frequency: 10 Hz, ablation time 30 min and in 20 ml of water. Analyzed with the spectrometer, as shown in Figure 5, the colloid presents a spectrum with a single maximum absorbance peak around 521.37 nm, which is why it is established that the AuNPs are spherical of approximately 25 nm in diameter, as found by Kumari & Meena (2000), in the study of synthesis of gold nanoparticles.

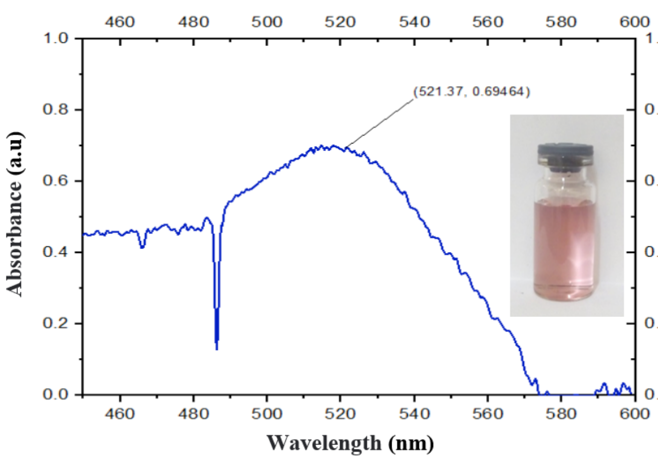

Figure 5. Absorption spectrum of AuNPs, prepared by the Pulsed Laser Ablation technique in water, corresponding to the colloids produced with 64.04 mJ/p in 30 min.

For the parameters: delay 115 μs, energy equivalent of 60.24 mJ/p, wavelength of 1064 nm, frequency 10 Hz, ablation time 30 min and 12 ml of water. Analyzed with the spectrometer, as shown in Figure 6, the colloid presents a spectrum with a single maximum absorbance peak around 520.19 nm, which is why it is established that the AuNPs are spherical of approximately 25 nm in diameter.

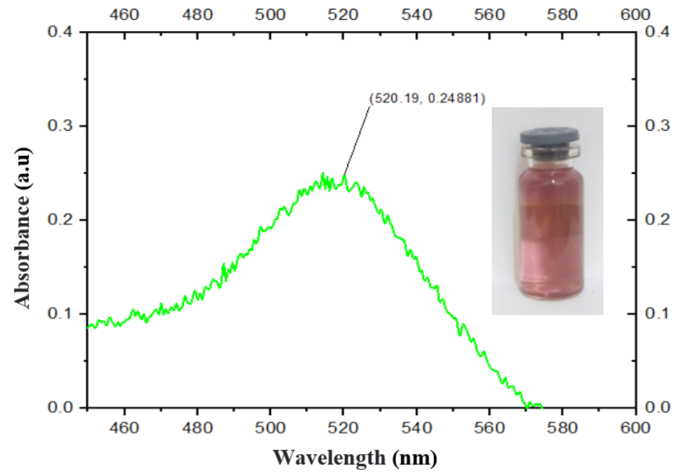

Figure 6. Absorption spectrum of AuNPs, prepared by the Pulsed Laser Ablation technique in water, corresponding to colloids produced with 60.24 mJ/p in 30 min.

- For the parameters: delay 115 μs equivalent in energy of 60.27 mJ/p, wavelength of 1064 nm, frequency 10 Hz, ablation time 50 min and 12 ml of water. Analyzed with the spectrometer, as shown in Figure 7, the colloid presents a spectrum with a single maximum absorbance peak around 521.95 nm, which is why it is established that the AuNPs are spherical of approximately 25 nm in diameter.

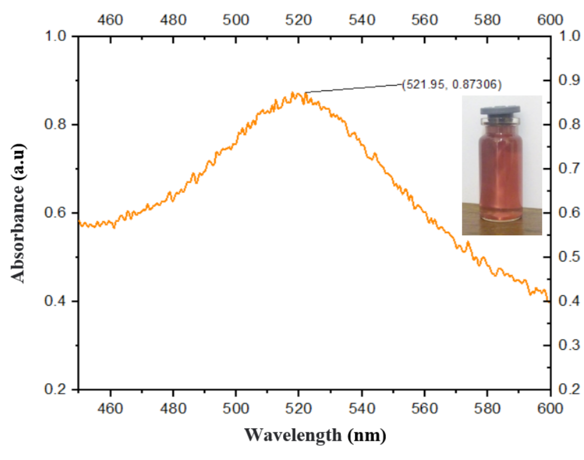

Figure 7. Absorption spectrum of AuNPs, prepared by the Pulsed Laser Ablation technique in water, corresponding to colloids produced with 60.27 mJ/p in 50 min.

For the parameters: delay 120 µs equivalent in energy of 56.50 mJ/p, wavelength of 1064 nm, frequency 10 Hz, ablation time 60 min and 12 ml of water. Analyzed with the spectrometer, as shown in Figure 8, the colloid presents a spectrum with a single maximum absorbance peak around 523.43 nm, for which it is established that the AuNPs are spherical of approximately 25 nm in diameter.

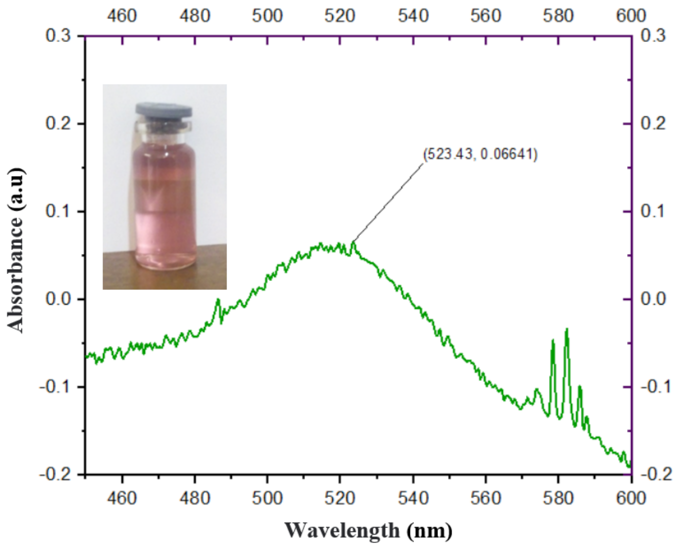

Figure 8. Absorption spectrum of AuNPs, prepared by the Pulsed Laser Ablation technique in water, corresponding to colloids produced with 56.50 mJ / p in 60 min.

The AuNPs were characterized by Transmission Electron Microscopy (TEM) with measurements at scales of 2 nm (Figure 9a), 50 nm (Figure 9b), 100 nm (Figure 10a), and 200 nm (Figure 10b).

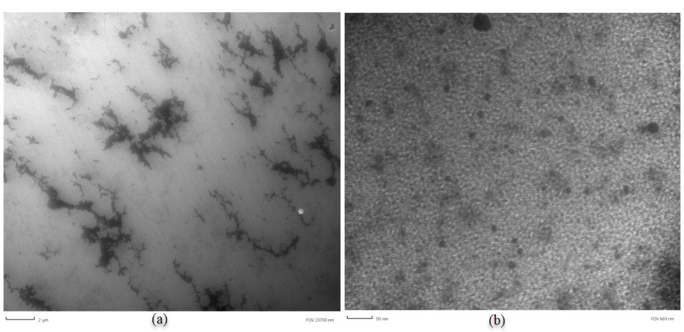

Figure 9. (a) TEM characterization of the AuNPs at 2 nm and (b) TEM characterization of the AuNPs at 50 nm.

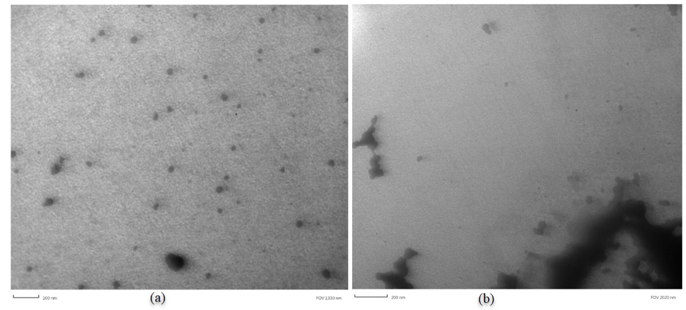

Figure 10. (a) TEM characterization of AuNPs at 100 nm and (b) TEM characterization of AuNPs at 200 nm.

From the results characterized by TEM, it is found that the AuNPs present a rough surface with lengths close to 25 nm and are suitable for functionalization with a group of amino acids.

The absorbance and wavelength of the different experiments allowed to calculate the average diameter and the concentration of the AuNPs. Replacing the data and fit parameters in equation 3, the diameter is obtained.

$$d = \frac{\ln\left(\frac{\lambda_{spr}-512}{6.53}\right)}{0.0216} \quad (3)$$

Replacing the experimental values and clearing from equation 2, we calculate the concentration () in equation 4.

$$c_{Au} = \left(\frac{A_{spr}(5.89 * 10^{-6})}{d * \exp(-4.75)}\right)^{1/0.314} \quad (4)$$

The result for five experiments it is presented in Table 1. Replacing the experimental data obtained in equations “3” and “4”, the values of Table 1 are obtained; where the AuNPs have a maximum peak wavelength close to 520 nm, which indicates that they are spherical gold nanoparticles of approximately 25 nm.

Table 1. Absorbance and wavelength at the maximum peak, average diameter and concentration of AuNPs, in colloidal state.

Experiment / Sample	Maximum peak absorbance (u.a.)	Wave-length at maxi-mum peak (nm)	Ave-rage dia-meter (nm)	Concen-tration
one	0.645	520.78	13.71	8.81E-06
two	0.701	521.37	16.72	4.70E-06
3	0.249	520.19	10.49	2.06E-05
4	0.066	523.43	25.92	1.18E-06
5	0.874	521.95	19.50	2.89E-06

By functionalizing AuNPs with the amino acid L-cysteine, the ability to detect heavy metals in water was studied. From the characterization of the synthesized material, the formation of nanoparticles encapsulated with L-cysteine presents characteristics that allow the detection of metal ions. The selectivity of the materials depends on the interaction of the adsorbent with the ions of the analyte material due to the specificity of the functional group present in the nanoparticles (Awual, et al., 2015). Electron relay in the optical properties of AuNPs depends mainly on the principle of localized surface plasmon resonance (LSPR). The functionalized AuNPs tend to interact with the ions of the analyte and give rise to the aggregation of the nanoparticles causing the color change from wine red to violet (Figure 11). In this study, cysteine participated as a reducing, stabilizing and chelating agent due to the presence of functional groups. Tripathi, et al. (2019)rapid, highly sensitive, and selective detection of lead. Colorimetric detection of lead using gold nanoparticles (AuNPs, reported that the zeta potential value of the free carboxylic group available on the surface of AuNPs can generate a net negative potential of -41.2 mV.

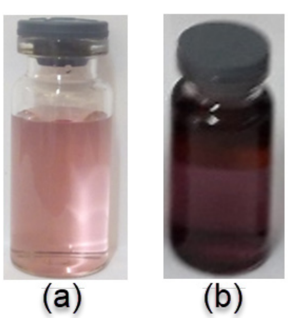

Figure 11. (a) Functionalized AuNPs and (b) AuNPs with analyte ion interactions.

The net negative charge caused by the functional group in AuNPs has an affinity towards the cationic nature of the analyte metal ions. For a better understanding, a UV-Vis analysis of the functionalized AuNPs activated by the analytes was carried out, having as a result that this amino acid tends to be absorbed with metal ions, especially with ions of Cd^{2+}, Pb^{2+}, and As^{2+} ions in high times. about 180 min, with Pb^{2+} being the one with the highest affinity (Han, et al., 2016).

CONCLUSIONS

The conclusions of this work are directed to the specific experimental conditions that were used for the production, and characterization of the colloids with gold nanoparticles produced, using the pulsed laser ablation technique in liquids, its characterization by UV-Visible spectroscopy, allows to conclude that the maximum absorbance of AuNPs is 520.78 nm, as it has only one maximum, then it is spherical nanoparticles. The bandwidth of the absorption spectrum shows that the nanoparticles are not homogeneous. The maximum peak centered at approximately 520 nm makes it possible to determine that the nanoparticles have a diameter of 25 nm, on average. From the results characterized by TEM, it is concluded that AuNPs present a rough surface with lengths close to 25 nm and are suitable for functionalization with a group of amino acids.

The gold nanoparticles were functionalized with L-cysteine at a 97% concentration, for applications in the detection of heavy metals in water: Cd^{2+}, Pb^{2+}, and As^{2+}. In the presence of these positive ions the color change of the colloids occurs, with which we can affirm that the heavy metals present in water are effectively detected.

REFERENCES

Alberti, G., Zanoni, C., Magnaghi, L. R., & Biesuz, R. (2021). Gold and Silver Nanoparticle-Based Colorimetric Sensors: New Trends and Applications. Chemosensors, 9 (11).

Avantes. (2018). UV-Vis-NIR Spectrometer - AvaSpec-ULS2048x64-EVO. https://www.medicalexpo.com/prod/avantes/product-104219-950813.html

Awual, M. R., Yaita, T., Suzuki, S., & Shiwaku, H. (2015). Ultimate selenium (IV) monitoring and removal from water using a new class of organic ligand based composite adsorbent. Journal of Hazardous Materials, 291, 111-119.

Bajorowicz, B., Kobylański, M. P., Gołḿbiewska, A., Nadolna, J., Zaleska-Medynska, A., & Malankowska, A. (2018). Quantum dot-decorated semiconductor micro-and nanoparticles: A review of their synthesis, characterization and application in photocatalysis. Advances in colloid and interface science, 256, 352-372.

De Mello Donegá, C. (2014). Nanoparticles: Workhorses of nanoscience. Springer.

Freestone, I., Meeks, N., Sax, M., & Higgitt, C. (2007). The Lycurgus cup — a roman nanotechnology. Gold bulletin, 40 (4), 270-277.

Freitas de Freitas, L., Costa Varca, G. H., Dos Santos Batista, J, G., & Benévolo Lugão, A. (2018). An overview of the synthesis of gold nanoparticles using radiation technologies. Nanomaterials, 8 (11).

Haiss, W., Thanh, N. T. K., Aveyard, J., & Fernig, D. G. (2007). Determination of size and concentration of gold nanoparticles from UV– Vis spectra. Analytical chemistry, 79 (11), 4215-4221.

Han, G., Wang, X., Hamel, J., Zhu, H., & Sun, R. (2016). Lignin-AuNPs liquid marble for remotely-controllable detection of Pb 2+. Scientific reports, 6 (1), 1-8.

Isaacoff, B. P., & Brown, K. A. (2017). Progress in top-down control of bottom-up assembly. ACS Publications.

Kaphle, A., Navya, PN, Umapathi, A., & Daima, HK (2018). Nanomaterials for agriculture, food and environment: applications, toxicity and regulation. Environmental chemistry letters, 16 (1), 43-58.

Kumari, P., & Meena, A. (2020). Green synthesis of gold nanoparticles from Lawsoniainermis and its catalytic activities following the Langmuir-Hinshelwood mechanism. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 606.

Moon, H., Lee, C., Lee, W., Kim, J., & Chae, H. (2019). Stability of quantum dots, quantum dot films, and quantum dot light-emitting diodes for display applications. Advanced Materials, 31 (34), 1804294.

Quantel. (2019). Q-smart 450 Pulsed Nd: YAG Laser, 213 to 1064nm, 8 to 450mJ, Product - Photonic Solutions, UK. https://www.photonicsolutions.co.uk/product-detail.php?prod=6345

Schaming, D., & Remita, H. (2015). Nanotechnology: from the ancient time to nowadays. Foundations of Chemistry, 17 (3), 187-205.

Soriano, M. L., Zougagh, M., Valcárcel, M., & Ríos, Á. (2018). Analytical Nanoscience and Nanotechnology: Where we are and where we are heading. Talanta, 177, 104-121.

Tripathi, R. M., Park, S. H., Kim, G., Kim, D. H., Ahn, D., Kim, Y. M, Kwon, S. J, Yoon, S.Y., Kang, H. J., & Chung, S. J. (2019). Metal-induced redshift of optical spectra of gold nanoparticles: An instant, sensitive, and selective visual detection of lead ions. International Biodeterioration & Biodegradation, 144.

Wahab, R., Ahmad, J., & Ahmad, N. (2019). Application of multi-dimensional (0D, 1D, 2D) nanostructures for the cytological evaluation of cancer cells and their bacterial response. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 583.

Yu, Y., Naik, S. S., Oh, Y., Theerthagiri, J., Lee, S. J., & Choi, M. Y. (2021). Lignin-mediated green synthesis of functionalized gold nanoparticles via pulsed laser technique for selective colorimetric detection of lead ions in aqueous media. Journal of Hazardous Materials, 420.