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Spectroscopic Detection of Glyphosate in Water Assisted by Laser-Ablated Silver Nanoparticles

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Abstract: Glyphosate is one of the most widely used herbicides in the world. Its safety for both human health and aquatic biomes is a subject of wide debate. There are limits to glyphosate's presence in bodies of water, and it is usually detected through complex analytical procedures. In this work, the presence of glyphosate is detected directly through optical interrogation of aqueous solution. For this purpose, silver nanoparticles were produced by pulsed laser ablation in liquids. Limits of detection of 0.9 mg/L and 3.2 mg/L were obtained with UV-Vis extinction and Surface Enhanced Raman spectroscopies, respectively. The sensing mechanism was evaluated in the presence of potential interferents as well as with commercial glyphosate-based herbicides.

Keywords: glyphosate; silver nanoparticle; colorimetry; SERS

1. Introduction

Glyphosate (*N*-(phosphonomethyl)glycine) is an effective broad-spectrum systemic herbicide successfully used worldwide for the control of undesirable weeds in cultures and gardens. The development of genetically modified crops resistant to glyphosate's effects as well as its patent expiration have contributed to its wide use in different formulations [1]. Glyphosate can be found in a ready-to-use diluted formulation containing adjuvants and surfactants, as well as in concentrations as high as 48% v/v requiring correct dilution by the end user prior to the application.

Glyphosate is mainly absorbed through the leaves of the plants, and then it is transported throughout the plant inhibiting the action of enzymes responsible by the amino acid synthesis. This metabolic pathway in plants is absent in animals, justifying the low toxicity attributed for the glyphosate [1]. However, some studies have shown that glyphosate can also affect enzymes present in animals [2,3]. In spite of its low mobility in soil, whereas it is adsorbed onto soil particles, glyphosate can be taken by rain into water bodies, compromising the ecosystem, mainly aquatic plants and its food chain dependents. Some techniques have been proposed to minimize environmental impacts, as fish and aquatic invertebrates are more sensitive than mammals to glyphosate. In this sense, bacteria and metals have been suggested as mediators to promote glyphosate degradation [4,5].

The use of glyphosate represents a risk to human health that has been previously discussed, considering residuals of the herbicide found in food [6] and also the consequences of water contamination. Some works have focused on the carcinogenicity of glyphosate [7] whereas others have indicated that the increase in the hardness of ground water by the accumulation of metal-glyphosate compounds may be the cause of renal disease [8]. Controversies about its toxicity are a setback in establishing a safety limit for glyphosate by international agencies. In Brazil, for example, the presence of glyphosate in drinking water is limited to 500 μg/L (3 μM) whereas the limit set for the environment is 65 μg/L (0.4 μM) [9,10]. The Brazilian regulatory agencies carry out periodic analyses following norms such as method 547 established by the United States Environmental Protection Agency (US EPA