

**SILVER NANOFLOWERS: ADSORPTION AND ULTRA-SENSITIVE
DETECTION OF ORGANIC POLLUTANTS IN SOLUTION VIA THE SERS
EFFECT**

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Silver nanoflowers (AgNFs) are branched metallic nanoparticles with a flower-like morphology, consisting of a spherical core with multiple petal-like protrusions. This structure provides a large surface area with an increased number of active sites for analyte interaction, while their metallic composition, rich in electromagnetic hot spots, enables strong amplification of the Raman signal of adsorbed molecules (SERS effect). As a result, AgNFs are considered promising substrates for detecting low concentrations of organic compounds[DP1.1]. In this context, the present study aims to synthesize and characterize AgNFs for future application as pollutant adsorbents and active SERS substrates. A bottom-up colloidal synthesis[1] was performed in aqueous medium under stirring and cooling, using AgNO₃ as the precursor, polyvinylpyrrolidone (PVP) as the stabilizing agent, and sodium citrate together with ascorbic acid as reducing agents. Excess PVP[2] was removed using NaBH₄, followed by successive washing steps with water/acetone mixtures, and the final material was oven-dried. Methylene blue (MB) was used as a probe molecule to simulate pollutant compounds, with tests performed by adding AgNFs to Eppendorf microtubes containing 0.25 mL of dye solution. The AgNFs were characterized by scanning electron microscopy (SEM), which

confirmed the flower-like nanoparticle morphology and porosity, and by BET analysis, which revealed a specific surface area of $4.387 \text{ m}^2 \text{ g}^{-1}$. Raman spectroscopy demonstrated significant signal enhancement of methylene blue in the presence of AgNF substrates, enabling calculation of the enhancement factor (EF), particularly at the 451 cm^{-1} band. Method sensitivity was confirmed by a limit of detection (LOD) of $7.8 \times 10^{-8} \text{ mol L}^{-1}$ and a limit of quantification (LOQ) of $1.1 \times 10^{-8} \text{ mol L}^{-1}$. These results indicate that the developed AgNFs are suitable for SERS-based applications. After confirming performance with methylene blue, additional tests were conducted using the pesticides glyphosate and 2,4-dichlorophenoxyacetic acid (2,4-D). However, the SERS spectra obtained were of low quality, with no detectable characteristic peaks. To address this limitation, AgNF surfaces were functionalized with anionic and cationic groups using mercaptoundecanoic acid (MUA) and choline chloride (SCC), respectively. SEM analyses indicated that the porous morphology was preserved after functionalization, while EDS and zeta potential measurements confirmed surface modification and acquisition of anionic and cationic charges. Nevertheless, Raman analyses with glyphosate (anionic), paraquat (cationic), and thiram (neutral) showed no significant differences between functionalized and non-functionalized AgNFs. An alternative adsorption method was therefore adopted, consisting of drop-casting the analyte solution directly onto the AgNFs followed by drying, using Eppendorf tube caps as supports. This procedure led to a significant improvement in Raman spectral quality, with the appearance of detectable peaks, although the support geometry limits analysis with a $10\times$ objective lens. Additional tests comparing solvents (100% water, 50% water/50% ethanol, and 100% ethanol) showed no relevant differences. Currently, adsorption in solution – similar to the methylene blue experiments – followed by drying and pellet pressing is being investigated to obtain a more uniform surface. SEM images indicate that pressing does not alter the porous morphology of the AgNFs. Raman tests using this new procedure are ongoing. We would like to thank INEO (FAPESP - processo nº 2025/27044-5.) and CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil) for financial support.

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