SURFACE BINDING PROPERTIES OF NATURAL DYES *CIS*-BIXIN AND *CIS*-NORBIXIN CAPPED SILVER NANOPARTICLES

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Surface interactions of spherical shaped Ag nanoparticles (NPs) coated with sodium borohydride were investigated with two natural dyes, *cis*-bixin and *cis*-norbixin, that are found in annatto. The changes in the surface plasmon absorption band of Ag NPs were used to understand the interaction. A red shift in the plasmon band was observed with the increase in the dye concentration for both molecules, confirming the surface capping. The changes occurring in the surface plasmon band in the presence of *cis*-bixin is different from that of *cis*-norbixin, indicating two different interactions. The degree of flocculation was quantified using semi-empirical flocculation parameters. The dependence of flocculation parameters with the concentration was investigated to determine the optimum concentration of the dye needed for the stabilization of Ag NPs.

Cis-bixin was extracted from achiote seeds, and *cis*-norbixin was synthesized from *cis*-bixin. Samples were characterized using high performance liquid chromatography, Fourier transform infrared spectroscopy and UV-visible spectroscopy to study the formation and purity. UV-visible spectroscopic data were used to characterize the Ag NPs coated with $NaBH_4$. It was found that Ag NPs had approximate particle sizes in the range 10-30 nm. Addition of *cis*-bixin showed a significant decrease in the absorbance of Ag NPs at 395 nm, and simultaneous increase in the absorbance for free bixin molecules at 484, 457 and 429 nm *via* a set of isosbestic points at 420 nm. This was an indication of rapid binding of bixin molecules with Ag NPs having 1:1 ratio with an association constant of 4.07×10^{4} mol^{-1} dm^{3}. Addition of *cis*-norbixin also showed a similar behavior with the decrease in absorbance of Ag NPs at 395 nm, and increase in absorbance at 479, 452 and 413 nm. Unlike bixin, two sets of isosbestic points appeared at 409 nm and 432 nm for norbixin, indicating rapid binding of norbixin to Ag NPs with two possible intermediates. This clearly confirmed that *cis*-norbixin molecules are getting capped onto the surface of Ag NPs with a 1:1 ratio for both intermediates having association constants of 3.34×10^{5} and 8.29×10^{5} mol^{-1} dm^{3}, respectively. The capping of *cis*-bixin and *cis*-norbixin onto the surface of Ag NPs significantly changed the extent of flocculation of the Ag NPs. As the concentration of dye increased, flocculation of Ag NPs increased for both dyes. However, the extent of flocculation of Ag NPs in the presence of norbixin is less compared to that of bixin. This is due to the higher electrostatic repulsion forces of the two caroxylic groups in norbixin molecules. The optimum concentrations of dye needed for stabilization of Ag NPs is 1.84×10^{-5} mol dm^{-3} for bixin; and 7.75×10^{-6} mol dm^{-3} for norbixin, respectively. The magnitude of the flocculation depends on the type of apocarotenoid and the concentration.

Keywords: *Cis*-bixin, *Cis*-norbixin, Flocculation, Silver nanoparticles.